PHYSICAL REVIEW B VOLUME 3, NUMBER 10 15 MAY 1971

Cluster Theory of the Electronic Structure of Disordered Systems*

Karl F. Freed† and Morrel H. Cohen
James Franck Institute, University of Chicago, Chicago, Illinois 60637
(Received 19 June 1970)

The equation of motion for the averaged Green's function in an alloy couples the latter to the Green's function for which the average is restricted so that the composition of one atom is held fixed. The average Green's function may be regarded as the Green's function for a zero-atom cluster, and it is coupled to the Green's function for a one-atom cluster. There is thus an infinite hierarchy of equations of motion in which the n-atom functions are coupled to the $(n+1)$ atom functions. The coherent potential approximation (CPA) of Soven corresponds to truncation in the equation of motion of the one-atom function. We have generalized the coherent potential theory to a theory of n-atom functions with truncation in the equation of motion of the $(n+1)$ atom function (CP$\vec{n}$). The formalism is developed, and specific formal results are reported. In particular, the existence of localized states in the band tails can be demonstrated, but the transition region from localized to extended states is beyond the reach of a cluster theory. The theory provides a systematic basis for quantitative improvement over the CPA, and allows for a discussion of the effects of randomness in the off-diagonal elements of the Hamiltonian. The cluster hierarchy is formally solved to provide a multiple-scattering expansion of the average Green's function, where terms involving one, two, etc., atom scattering are grouped together. This expansion can be used to generate recently proposed generalizations of the CPA, but when used in conjunction with the self-consistent n-atom functions of the CP$\vec{n}$, it provides the best approximate averaged Green's function for which the lowest-order corrections involve the scattering from compact $(n+1)$ atom clusters.

I. INTRODUCTION

Apart from strongly ionic or molecular materials or from simple metals, our present knowledge of the electronic structures of condensed materials is rudimentary except for crystals. There, structural periodicity leads to the remarkable simplicity of the electronic wave functions expressed in the Bloch-Floquet theorem and to the existence of energy bands. Our present concern is with the corresponding universal features of the electronic structures of disordered materials. Soven and others[1] have developed the coherent potential approximation (CPA) into a quantitative tool for the study of the electronic structures of simple alloys. It yields, however, only bands of extended states with sharp edges and shows signs of inaccuracy at the band edges. In amorphous semiconductors, the band edges must play a central role in determining the electronic properties. Moreover, on both theoretical and empirical grounds it seems highly plausible that the electronic structure of disordered materials consists of bands of extended states with tails of localized states which may, in fact, overlap.[2] The character of the wave functions changes from extended to localized at an energy E_c near each band edge, where the carrier mobility drops abruptly.[2] One of the central tasks of the electron theory of disordered materials is to substantiate or correct these models.[3] Accordingly, we have addressed ourselves to improving the CPA qualitatively and quantitatively to the point where it can conceivably contain such features as tails of localized states and mobility edges.[2] The resulting quantitative improvement of the CPA would be useful for simple alloys.

Electronic properties of a disordered material which are associated with the entire system, e.g., the density of states, contain within them a sampling of all configurations in the system. In calculating such properties, therefore, it is admissible to carry out averages over an ensemble of systems having all possible configurations. Various approximations differ in the way the ensemble average is inserted into the structure of the calculation. In the CPA in particular, the average is carried out in such a way that the effective potential experienced by an electron is the same on each site. However, localized states produced by a single impurity are associated with the deviation of the potential introduced by the impurity from that of the perfect crystal. Similarly, localized states in disordered materials are associated with the fluctuations in the total potential, i.e., with the variation in potential from site to site. This is readily seen from the arguments of Lifshitz, Kane, Halperin and Lax, Zittartz and Langer, and particularly of Ziman in the context of a classical percolation calculation.[4] The CPA considers the response of an electron to the potential at a single site. The minimal improvement over the CPA would therefore be to consider the response of the electron to the potential on two adjacent sites before averaging, which allows for response of the electron to the difference in potential between the two sites.[5] This suggests in turn the possibility of considering the response of the electron to a cluster of n atoms of fixed composition and/or position, treating the rest of the material in an averaged way (CP$\vec{n}$).

Bound states can result when the potential difference between the cluster and the averaged environment becomes large enough. One might hope in this way to obtain some exact results by allowing the cluster size to approach infinity. However, it then no longer becomes possible to distinguish between an extended state and one localized on a cluster. The vexing problem of the quantitative description of the transition region between localized and extended states, which is central to the theory of disordered semiconductors, is therefore inaccessible to the cluster approach. As we shall discuss later, the difficulty is the same one encountered in the theory of phase transitions.[6] Nevertheless, one could expect to obtain improvements over the CPA in the main body of the band and some semiquantitative results for the band tails as well. Accordingly, we develop in the present paper a systematic cluster theory of Green's functions in disordered systems via a hierarchy of approximations containing the usual CPA as its lowest order.

As Edwards notes, in order to obtain localized states in the translationally invariant averaged system, it is necessary to break the symmetry in some manner. This symmetry breaking is analogous to that which is required, for instance, in order to obtain ferromagnetism.[6] Thus, the use of a fixed cluster of atoms is a particular choice of symmetry breaking which is expected to accurately reproduce some properties of localized states. In discussing localized states in disordered systems, Anderson[4] similarly breaks symmetry by focusing attention upon a specific lattice site. By focusing on a particular cluster of atoms we, of course, obtain results which are not translationally invariant. The theories of Lifshitz and Ziman are also manifestly not translationally invariant.[4] No attempt is made by Anderson, Lifshitz, or Ziman to restore the required translational invariance to prove that the localized states are not destroyed when this invariance is reintroduced. It is therefore necessary to introduce averaging procedures which restore the requisite translational invariance. This enables us to show that the localized states obtained from the translationally noninvariant theory do not become Mott-type extended resonances[2] when this invariance is restored. For this purpose only the simplest averaging procedure is necessary. The first and simplest approach, which involves appropriate averaging over the random potential on the cluster and the location of the cluster, provides a great deal of insight as to the nature of bound states in the band tails. Alternatively, the cluster hierarchy can formally be solved for the average Green's function in a manifestly translationally invariant form which is a highly summed version of the usual multiple-scattering theories that have been employed in connection with the CPA.[1] In this expansion, terms are classified as involving the scattering from m-atom clusters, $m=0$, 1, 2, ..., N. Upon introduction of the approximate self-consistent n-cluster Green's functions (CP$\vec{n}$), the resulting approximate averaged Green's function is such that the lowest-order corrections involve scattering from compact $(n+1)$ atom clusters.

II. CLUSTER HIERARCHY

A. Definitions and Conditional Averaging

We work throughout in the one-electron approximation. The disorder appears in the one-electron part of the many-electron Hamiltonian, and all of the basic modifications of the electronic structure therefore occur already in the one-electron approximation. Many-body effects can be inserted once the single-particle problem is understood.

The Green's function $\mathcal{G}$ for an electron in a material with a given unaveraged configuration and a Hamiltonian H_0+V is defined by

$$(E-H_0-V)\,\mathcal{G}(E)=1\ , \qquad (2.1)$$

where E is the electron energy, the representation for $\mathcal{G}$ is left unspecified, and the right-hand side is the unit operator. We assume that H_0+V is time independent, but the theory may be easily generalized to include, e.g., the time dependence associated with atomic motion in a classical fluid. In the Hamiltonian, H_0 relates to some reference state about which the system fluctuates, and V is the potential of fluctuation, which we take to be random.

For many electronic properties of the entire material, it is sufficient to know only the average $G_0(E)$ of $\mathcal{G}(E)$ over all configurations of the system, i.e., over the random potential V, as discussed in the Introduction:

$$G_0(E)=\langle\,\mathcal{G}(E)\rangle\ . \qquad (2.2)$$

Here and throughout, $\langle\,\rangle$ implies an average over V. Equation (2.2) suffices for the density of states; conductivity would require $\langle\,\mathcal{G}\mathcal{G}\,\rangle$, the Hall constant $\langle\,\mathcal{G}\mathcal{G}\mathcal{G}\rangle$, etc.[1] We confine ourselves to $\langle\,\mathcal{G}\rangle$.

However, in order to assess the nature of the states which contribute to $\langle\,\mathcal{G}(E)\rangle$ in a given range of energy, whether localized or extended, it is necessary to understand what particular configurations of the random potential gives rise to them. This can be done by examining the Green's functions for a material in which the contribution to the potential V of a cluster of atoms is fixed by specifying the positions and compositions of the atoms within the cluster and averaging those for all atoms outside. We therefore decompose the potential into a contribution from a cluster $\vec{n}$ (the symbol $\vec{n}$ implies the specification of position and composition of n atoms), $V_{\vec{n}}$ and into a contribution from the remainder of the N atoms in the material, $V_{\vec{N}-\vec{n}}$

$$V = V_{\vec{n}} + V_{\vec{N}-\vec{n}} \; . \tag{2.3}$$

Let $\langle\,\rangle^{\vec{m}}$ imply an average over only the parameters of the cluster $\vec{m}$ and $\langle\,\rangle_{\vec{l}}$ an average over those of all atoms outside $\vec{l}$, so that

$$\langle\,\rangle_{\vec{l}} = \langle\,\rangle^{\vec{N}-\vec{l}} \; . \tag{2.4}$$

The Green's function for a material in which the cluster $\vec{n}$ is specified and the rest averaged may then be written as

$$G_{\vec{n}} = \langle \mathcal{G} \rangle_{\vec{n}} \equiv \langle \mathcal{G} \rangle^{\vec{N}-\vec{n}} \; . \tag{2.5}$$

It is often convenient to specify separately one atom $\vec{\alpha}$ of an $(n+1)$ atom cluster by the correspondence $\vec{n}+\vec{1} \leftrightarrow \vec{n}, \; \vec{\alpha}$.

B. Equations of Motion

The equation of motion for $G_{\vec{n}}$ is obtained by averaging that for $\mathcal{G}$, (2.1), over the potential $V_{\vec{N}-\vec{n}}$,

$$\langle (E - H_0 - V_{\vec{n}} - V_{\vec{N}-\vec{n}})\, \mathcal{G} \rangle_{\vec{n}} = 1 \; . \tag{2.6}$$

Using the definitions of Sec. II A, this may be rewritten as

$$(E - H_0 - V_{\vec{n}})\, G_{\vec{n}} - \langle V_{\vec{N}-\vec{n}}\, \mathcal{G} \rangle_{\vec{n}} = 1 \; . \tag{2.7}$$

In many cases of interest, the potential V is a linear superposition of contributions from each of the atoms (or molecules) in the material so that

$$V = \sum_{\vec{\alpha} \in \vec{N}} V_{\vec{\alpha}} \; , \tag{2.8}$$

and in particular

$$V_{\vec{N}-\vec{n}} = \sum_{\vec{\alpha} \in \vec{N}-\vec{n}} V_{\vec{\alpha}} \; . \tag{2.9}$$

This permits simplification of (2.7) to

$$(E - H_0 - V_{\vec{n}})\, G_{\vec{n}} - \sum_{\vec{\alpha} \notin \vec{n}} \langle V_{\vec{\alpha}}\, G_{\vec{n}\vec{\alpha}} \rangle^{\vec{\alpha}} = 1 \; . \tag{2.10}$$

The set of equations of motion (2.10) for cluster Green's functions of all orders n has a hierarchial form (Taylor[1]) reminiscent of that occurring in many-body theory in that the equation for $G_{\vec{n}}$ contains $G_{\vec{n}+\vec{1}}$. The hierarchy terminates only at $\vec{n} = \vec{N}$, when $G_{\vec{N}} = \mathcal{G}$. Explicit but approximate results can be obtained by truncating the hierarchy at some smaller $\vec{n}$, and a specific and simple truncation scheme is introduced and discussed in Sec. III. We prepare for the truncation scheme and for a few exact results developed later by introducing the proper self-energy $\sigma\,(E)$ and related quantities.

C. Proper Self-Energies

The proper self-energy $\sigma_{\vec{n}}$ associated with $G_{\vec{n}}$ is defined through

$$(E - H_0 - V_{\vec{n}} - \sigma_{\vec{n}})\, G_{\vec{n}} = 1 \tag{2.11}$$

in the present formalism. Comparing (2.11) and (2.10) shows that

$$\sigma_{\vec{n}} = \sum_{\vec{\alpha} \notin \vec{n}} \sigma_{\vec{n}}^{(\alpha)} \; , \tag{2.12}$$

where

$$\sigma_{\vec{n}}^{(\vec{\alpha})}\, G_{\vec{n}} \equiv \langle V_{\vec{\alpha}}\, G_{\vec{n},\vec{\alpha}} \rangle^{\vec{\alpha}} \; , \tag{2.13}$$

and the parentheses around the superscript α in $\sigma_{\vec{n}}^{(\alpha)}$ indicate that an average has been taken over the parameters for atom α.

It is now convenient to introduce the general scattering, or T-matrix $T_{\vec{n}}^{\vec{\alpha}}$ relating $G_{\vec{n}}$ to $G_{\vec{n},\vec{\alpha}}$,

$$G_{\vec{n},\vec{\alpha}} = G_{\vec{n}} + G_{\vec{n}}\, T_{\vec{n}}^{\vec{\alpha}}\, G_{\vec{n}} \; . \tag{2.14}$$

The physical significance of $T_{\vec{n}}^{\vec{\alpha}}$ will be made clear shortly. Substituting (2.14) into (2.13) gives a somewhat simpler form for $\sigma_{\vec{n}}^{(\alpha)}$,

$$\sigma_{\vec{n}}^{(\alpha)} = \langle V_{\vec{\alpha}} + V_{\vec{\alpha}}\, G_{\vec{n}}\, T_{\vec{n}}^{\vec{\alpha}} \rangle^{\vec{\alpha}} \; . \tag{2.15}$$

Comparing the equations of motion for $G_{\vec{n}}$ and $G_{\vec{n},\vec{\alpha}}$ in the forms (2.11) with the definition (2.14) of $T_{\vec{n}}^{\vec{\alpha}}$ shows that $T_{\vec{m}}^{\vec{\alpha}}$ may be related to an effective scattering potential $U_{\vec{m}}^{\vec{\alpha}}$ in the usual way that T matrices are related to scattering potentials:

$$T_{\vec{m}}^{\vec{\alpha}} = U_{\vec{m}}^{\vec{\alpha}}\, (1 - G_{\vec{m}}\, U_{\vec{m}}^{\vec{\alpha}})^{-1} \; , \tag{2.16}$$

where

$$U_{\vec{m}}^{\vec{\alpha}} = V_{\vec{\alpha}} + \sigma_{\vec{m},\vec{\alpha}} - \sigma_{\vec{m}} \; . \tag{2.17}$$

The effective potential $U_{\vec{m}}^{\vec{\alpha}}$ is simply the difference between cluster potential and self-energy in the equation of motion for the "perturbed" Green's function $G_{\vec{m},\vec{\alpha}}$ and that for the "unperturbed" Green's function $G_{\vec{m}}$. More explicitly, $U_{\vec{m}}^{\vec{\alpha}}$ is given by

$$U_{\vec{m}}^{\vec{\alpha}} = V_{\vec{\alpha}} - \sigma_{\vec{m}}^{(\alpha)} + \sum_{\beta \notin \vec{m},\vec{\alpha}} (\sigma_{\vec{m},\vec{\alpha}}^{(\beta)} - \sigma_{\vec{m}}^{(\beta)}) \; . \tag{2.18}$$

Before going on to discuss approximate truncation of the hierarchy, we introduce a condition which must be satisfied by $T_{\vec{m}}^{\vec{\alpha}}$ within any approximation scheme. Any lower-order Green's function must be obtainable by averaging down a higher-order Green's function, the cluster for which contains the lower-order cluster, and in particular,

$$\langle G_{\vec{m},\vec{\alpha}} \rangle^{\vec{\alpha}} \equiv G_{\vec{m}} \; . \tag{2.19}$$

Averaging (2.14) over the parameters of $\vec{\alpha}$ and inserting (2.19) yields the self-consistency condition

$$\langle T_{\vec{m},\vec{\alpha}} \rangle^{\vec{\alpha}} \equiv 0, \quad \text{all } \vec{m}, \; \vec{\alpha} \notin \vec{m} \; . \tag{2.20}$$

III. TRUNCATION: GENERALIZATION OF CPA

We are concerned with an exceedingly complex problem. An electron is moving according to a Hamiltonian H_0, which may be periodic or translation invariant, while being scattered by a random set of scattering centers. The scattering potential from each center may be strong, the centers may be densely distributed, and the contributions to V from each may overlap. One class of attempts to solve similar multiple-scattering problems involves replacement of the actual scattering potential by a mean field having the translational symmetry of the averaged system. Such an approach can be exact in principle. The mean field then becomes identical to the proper self-energy, e.g., in Eq. (2.11) for G_0.[1] From this point of view, all mean field theories contain approximations to the self-energy of varying degrees of accuracy. The simplest approximation is to replace the random potential V by its average $\langle V \rangle$, the virtual crystal approximation.[7] As long as the potential fluctuations are sufficiently small, i.e., $V - \langle V \rangle$ small in some sense, for perturbation theory in powers of $V - \langle V \rangle$ to converge rapidly, the virtual crystal approximation works reasonably well. For a density of scatterers, sufficiently low that multiple scattering can be ignored and single scattering treated exactly, the optical model works well.[8] Soven[1] has introduced a scheme, the CPA (Taylor[1]), which combines the virtues of both of the above and gives reasonably accurate results for high densities of scatterers in the main body of the energy band of a disordered alloy. However, all of the above simplify the proper self-energy so greatly that the resulting energy bands no longer contain tails of localized states. Even the CPA, the most complete of these, omits the spatial nonlocality of the proper self-energy. Soven has shown explicitly that the higher-order corrections to the CPA are largest at the band edges, where such omissions are most serious. However, higher-order perturbative corrections which themselves preserve the analytic structure of the lower-order theory will not lead to the missing band tails.

There is ample evidence that these band tails come from potential fluctuations,[4] some of which would be automatically included in the clusters present in the conditionally averaged systems we have discussed in the last section. For the cluster Green's function $G_{\vec{n}}$, only contributions to the self-energy from the N-n atoms α outside the cluster $\sigma_{\vec{n}}^{(\alpha)}$ need be replaced by mean fields. There is thus some hope that bound states can be preserved in an approximation scheme developed via the cluster hierarchy. We therefore generalize the CPA to describe the motion of an electron in the presence of a specified, i.e., unaveraged, cluster $\vec{n}$ and an approximate but self-consistent mean field contributed by the remaining N-n atoms over which averages have been taken.

As a first step in developing our approximation scheme, we rederive the CPA within the framework of our cluster hierarchy[1] in a manner that immediately provides the necessary clues to its desired generalization. In addition, we give an alternative derivation of the CPA[1] to illustrate how its cluster generalization, which we subsequently give, is superior to perturbative correction of the CPA.

A. CPA

The CPA[1] is concerned with the totally averaged Green's function G_0, which may be regarded as the zero-order member of our hierarchy of the cluster Green's functions. In all the cases that we consider, G_0 has translational invariance. Since G_0 is related to the self-energy $\sigma_{\vec{0}}$ through

$$(E - H_0 - \sigma_{\vec{0}})\, G_0 = 1 \qquad (3.1)$$

[cf. Eq. (2.11)], where

$$\sigma_{\vec{0}} = \sum_\alpha \sigma_0^{(\alpha)} , \qquad (3.2)$$

$\sigma_0^{(\alpha)}$ is independent of α up to a translation. The problem reduces to finding the single operator $\sigma_0^{(\alpha)}$. To do so approximately, it is sufficient to truncate the cluster hierarchy at some point. The equation of motion for G_0 involves in addition only G_1. Thus, within the framework provided by our cluster hierarchy, the least accurate kind of approximation would involve truncation at G_1. This is most readily effected by utilizing the corresponding T matrix $T_0^{\vec{\alpha}}$.

The T matrix by means of which G_1 can be constructed from G_0 according to Eq. (2.14) is given by

$$T_0^{\vec{\alpha}} = U_0^{\vec{\alpha}} (1 - G_0 U_0^{\vec{\alpha}})^{-1} , \qquad (3.3)$$

where

$$U_0^{\vec{\alpha}} = V_{\vec{\alpha}} - \sigma_0^{(\alpha)} + \sum_{\beta \neq \alpha} (\sigma_{\vec{\alpha}}^{(\beta)} - \sigma_0^{(\beta)}) , \qquad (3.4)$$

according to Eqs. (2.16) and (2.18), respectively. Now $\sigma_{\vec{\alpha}}^{(\beta)}$ is the proper self-energy from atom β where atom $\vec{\alpha}$ has its parameters fixed, whereas in $\sigma_0^{(\beta)}$ the parameters of atom α have been averaged over. It is physically reasonable that there is a finite distance, a coherence length, over which the effect of fixing atom α can persist. If one supposes that coherence length to be less than an interatomic separation, which means no persistence at all, one can set

$$\sigma_{\vec{\alpha}}^{(\beta)} \Rightarrow \sigma_0^{(\beta)}, \quad \alpha \neq \beta \ \text{(CPA)}. \qquad (3.5)$$

Insertion of (3.5) into (3.4) yields

$$U_0^{\vec{\alpha}} = V_{\vec{\alpha}} - \sigma_0^{(\alpha)} , \tag{3.6}$$

and insertion of (3.6) into (3.3) yields[1]

$$T_0^{\vec{\alpha}} = (V_{\vec{\alpha}} - \sigma_0^{(\alpha)})[1 - G_0(V_{\vec{\alpha}} - \sigma_0^{(\alpha)})]^{-1} \quad \text{(CPA)} . \tag{3.7}$$

Finally, insertion of the approximate form (3.7) into the self-consistency condition

$$\langle T_0^{\vec{\alpha}} \rangle^{\vec{\alpha}} = 0 \tag{3.8}$$

following from (2.20), yields the CPA. The coherent potential is clearly seen as an approximation to $\sigma_{\vec{0}}$.

Within the present theoretical framework, the CPA follows from truncating the cluster Green's-function hierarchy at G_1 by ignoring the outward persistence of the effect of fixing the parameters of an atom $\vec{\alpha}$ upon the proper self-energy (Taylor[1]). This provides a clear mathematical and physical basis for the CPA. It can be expected to work best either when the fluctuating potentials are weak, so that the outward propagation of the effect of conditional averaging is also weak, or when the mean free path, which relates directly to the coherence length, is fairly short. A condition of this sort is required for the validity of the generalizations of the CPA that we shall introduce later. However, at the mobility edge, the energy of the transition from localized to extended states,[9] it is the persistence of the amplitude of a wave function over the entire material which distinguishes an extended from a localized state.[10] Distinctions of this sort cannot be explored within a theory which ignores correlations persisting beyond a certain distance.

Within the CPA, the average T matrix for scattering off-site α with site $\vec{\beta}$ specified does not vanish as it should[1]:

$$\langle T_{\vec{\beta}}^{\vec{\alpha}} \rangle^{\vec{\alpha}} \neq 0 \quad \text{(CPA)}, \tag{3.9}$$

where[1]

$$T_{\vec{\beta}}^{\vec{\alpha}} \equiv (V_{\vec{\alpha}} - \sigma_0^{(\alpha)})[1 - G_0^{\vec{\beta}}(V_{\vec{\alpha}} - \sigma_0^{(\alpha)})]^{-1} \quad \text{(CPA)} \tag{3.10}$$

and[1]

$$G_0^{\vec{\beta}} = [\, G_0^{-1} - (V_{\vec{\beta}} - \sigma_0^{(\beta)})]^{-1} \quad \text{(CPA)} . \tag{3.11}$$

The correction terms to G_0 which would make (3.9) vanish are the lowest-order correction terms within our cluster hierarchy. What may be regarded as approximations to these have been found to be significant near the band edges.[1]

We can see that averaging Eq. (3.7) leads to an α independent $\sigma_0^{(\alpha)}$ up to a translation which is local in space and is complex only within a bounded energy domain. The total self-energy $\sigma_{\vec{0}}$ is therefore $\vec{k}$ independent, which leads immediately to sharp band edges, i.e., no tails of localized states.

The above derivation of the CPA imbeds it within the hierarchy of cluster Green's functions that we have introduced and provides a basis for its generalization. An alternative derivation, which we now introduce, makes clearer the connection with Soven's original derivation.[1] We develop the exact Green's function $\mathcal{G}$ about some as yet unspecified Green's function $\mathcal{G}_0$, defining thereby a T matrix

$$\mathcal{G} = \mathcal{G}_0 + \mathcal{G}_0 T \mathcal{G}_0 , \tag{3.12a}$$

$$\mathcal{G} = (E - H_0 - \textstyle\sum_\alpha V_{\vec{\alpha}})^{-1} , \tag{3.12b}$$

$$\mathcal{G}_0 = (E - H_0 - \textstyle\sum_\alpha W^{(\alpha)})^{-1} , \tag{3.12c}$$

where the $W^{(\alpha)}$ and therefore $\mathcal{G}_0$ are as yet unspecified but are not random variables. Equations (3.12) lead to the following explicit expression for T:

$$T = U(1 - \mathcal{G}_0 U)^{-1} , \tag{3.13a}$$

$$U = \textstyle\sum_\alpha (V_{\vec{\alpha}} - W^{(\alpha)}) . \tag{3.13b}$$

Averaging $\mathcal{G}$ in (3.12a) completely to obtain the exact G_0 leads to

$$G_0 = \mathcal{G}_0 + \mathcal{G}_0 \langle T \rangle \mathcal{G}_0 . \tag{3.14}$$

Imposing the condition that the reference Green's function $\mathcal{G}_0$ be the exact averaged Green's function G_0 leads to

$$\langle T \rangle = 0 , \tag{3.15}$$

with the result that the reference potential $W^{(\alpha)}$ becomes the exact self-energy $\sigma_0^{(\alpha)}$. This $\sigma_0^{(\alpha)}$ can, in principle, be determined by the self-consistent solution of

$$\langle T \rangle = 0 = \langle \textstyle\sum_\alpha (V_{\vec{\alpha}} - \sigma_0^{(\alpha)})[1 - G_0 \textstyle\sum_\alpha (V_{\vec{\alpha}} - \sigma_0^{(\alpha)})]^{-1} \rangle , \tag{3.16}$$

but it is practically impossible to do so. Instead, and at this point we follow Soven by making an individual-atom t-matrix expansion of (3.16) with G_0 replaced by the as yet unspecified $\mathcal{G}_0$, we write

$$\langle T \rangle = \langle \sum_\alpha t_{\vec{\alpha}} + \sum_{\beta \neq \alpha} t_{\vec{\alpha}} \mathcal{G}_0 t_{\vec{\beta}} + \cdots \rangle , \tag{3.17a}$$

$$t_{\vec{\alpha}} = (V_{\vec{\alpha}} - W^{(\alpha)})[1 - \mathcal{G}_0 (V_{\vec{\alpha}} - W^{(\alpha)})]^{-1} . \tag{3.17b}$$

We note that $t_{\vec{\alpha}}$ depends only on single-atom quantities. If the $V_{\vec{\alpha}}$ are all independent random variables, then

$$\langle T \rangle = \sum_\alpha \langle t_{\vec{\alpha}} \rangle^{\vec{\alpha}} + \sum_{\beta \neq \alpha} \langle t_{\vec{\alpha}} \rangle^{\vec{\alpha}} \mathcal{G}_0 \langle t_{\vec{\beta}} \rangle^{\vec{\beta}} + \cdots . \tag{3.17c}$$

At this point, Soven determines $W^{(\alpha)}$ to be the coherent potential by imposing the requirement that the single-atom t matrices vanish when averaged,[1]

$$\langle t_{\vec{\alpha}} \rangle^{\alpha} = 0 \quad \text{(CPA)} , \tag{3.18a}$$

so that[1]

$$G_0 = \mathcal{G}_0 + \text{neglected terms of fourth and higher order in } t_{\vec{\alpha}} \quad \text{(CPA)} . \tag{3.18b}$$

We see that $\langle T \rangle$ does not vanish in the CPA but that the leading terms are of fourth order in the $t_{\vec{\alpha}}$.[1] Finally, we see also that the CPA cannot be improved near the band edges by direct calculation of the higher terms in (3.18b) because all have the same analytic structure and give rise to sharp band edges. As noted in Sec. I, the cluster hierarchy can be used to generate a summed version of the t-matrix expansion of (3.17a). This expansion is presented in Sec. VI, and its relation to the cluster theory is discussed.

Although all calculations employing the CPA have been performed when V_α can only have two values,[1] the above general formalism is not restricted to this case. Thus, the random variables V_α could take on a large number of discrete values, or even have a continuous distribution. Thus, the following theoretical development is not limited to the case of binary alloys.

B. Coherent Cluster Potentials

In our first derivation of the CPA, the key approximation was (3.5) and the corresponding self-energy was determined from (3.7) and (3.8). The CPA can therefore be generalized to the corresponding approximation (CP$\vec{n}$) for a cluster Green's function of order n ($n>0$) as follows:

$$\sigma^{(\beta)}_{\vec{n},\vec{\alpha}} \Rightarrow \sigma^{(\beta)}_{\vec{n}}, \quad \text{all } \beta \notin \vec{n}, \vec{\alpha} \quad (\mathrm{CP}\vec{n}) \tag{3.19a}$$

$$T^{\vec{\alpha}}_{\vec{n}} = (V_{\vec{\alpha}} - \sigma^{(\alpha)}_{\vec{n}})[1 - G_{\vec{n}}(V_{\vec{\alpha}} - \sigma^{(\alpha)}_{\vec{n}})]^{-1} \quad (\mathrm{CP}\vec{n}), \tag{3.19b}$$

$$\langle T^{\vec{\alpha}}_{\vec{n}} \rangle^{\vec{\alpha}} = 0 \quad (\mathrm{CP}\vec{n}). \tag{3.19c}$$

As is shown in Sec. IV, (3.19c) is a single *algebraic* equation for each $\vec{\alpha}$ within the coherence range of the cluster $\vec{n}$. This is, of course, an important simplifying feature in any attempt to perform numerical calculations. However, if the $\sigma^{(\alpha)}_{\vec{n}}$ in (3.19b) and (3.19c) were different for all $\alpha \notin \vec{n}$, then the problem of the evaluation of $G_{\vec{n}}$ via (2.11) would be as complicated as that of evaluating $\mathcal{G}$ of (2.1) for a particular irregular composition of the whole lattice, thereby making CP$\vec{n}$ intractable. In Sec. IV, we therefore prove that $\sigma^{(\alpha)}_{\vec{n}}$ differs only from its asymptotic value $\sigma^{(\alpha)}_{A}$ inside a region about the cluster $\vec{n}$ whose size is of the order of the coherence length. Therefore, for the cases of interest where the coherence length is short, the evaluation of $G_{\vec{n}}$ is of comparable difficulty to the evaluation of a Green's function for an impurity cluster (of the size of the coherence length) in a pure crystal (with complex band structure). Before proving the above properties and demonstrating other explicit results which imply the feasibility of CP$\vec{n}$ calculations, we consider an alternate derivation of CP$\vec{n}$ which parallels Soven's derivation of CPA.[1]

Alternatively, we can develop $\mathcal{G}$ about a reference function $\mathcal{G}_{\vec{n}}$, defining thereby a $T_{\vec{n}}$

$$\mathcal{G} = \mathcal{G}_{\vec{n}} + \mathcal{G}_{\vec{n}} T_{\vec{n}} \mathcal{G}_{\vec{n}}, \tag{3.20a}$$

$$\mathcal{G}_{\vec{n}} = \Big(E - H_0 - V_{\vec{n}} - \sum_{\alpha \notin \vec{n}} W^{(\alpha)}_{\vec{n}}\Big)^{-1}, \tag{3.20b}$$

$$T_{\vec{n}} = U_{\vec{n}}(1 - \mathcal{G}_{\vec{n}} U_{\vec{n}})^{-1}, \tag{3.20c}$$

$$U_{\vec{n}} = \sum_{\alpha \notin \vec{n}} (V_{\vec{\alpha}} - W^{(\alpha)}_{\vec{n}}). \tag{3.20d}$$

Averaging (3.20a) over all but the cluster $\vec{n}$ gives

$$G_{\vec{n}} = \mathcal{G}_{\vec{n}} + \mathcal{G}_{\vec{n}} \langle T_{\vec{n}} \rangle_{\vec{n}} \mathcal{G}_{\vec{n}}. \tag{3.21}$$

A single-atom t-matrix expansion of $T_{\vec{n}}$ gives

$$T_{\vec{n}} = \sum_{\alpha \notin \vec{n}} t^{\vec{\alpha}}_{\vec{n}} + \sum_{\alpha \neq \beta \notin \vec{n}} t^{\vec{\alpha}}_{\vec{n}} \mathcal{G}_{\vec{n}} t^{\vec{\beta}}_{\vec{n}} + \cdots, \tag{3.22a}$$

where

$$t^{\vec{\alpha}}_{\vec{n}} = (V_{\vec{\alpha}} - W^{(\alpha)}_{\vec{n}})[1 - \mathcal{G}_{\vec{n}}(V_{\vec{\alpha}} - W^{(\alpha)}_{\vec{n}})]^{-1}. \tag{3.22b}$$

The CP$\vec{n}$ approximation is

$$G_{\vec{n}} \Rightarrow \mathcal{G}_{\vec{n}} \quad (\mathrm{CP}\vec{n}), \tag{3.23a}$$

with

$$\langle t^{\vec{\alpha}}_{\vec{n}} \rangle^{\vec{\alpha}} = 0, \quad \text{all } \alpha \notin \vec{n} \quad (\mathrm{CP}\vec{n}) \tag{3.23b}$$

determining the cluster coherent potential

$$W^{(\alpha)}_{\vec{n}} \Rightarrow \sigma^{(\alpha)}_{\vec{n}} \quad (\mathrm{CP}\vec{n}). \tag{3.23c}$$

Thus, in the CP$\vec{n}$ $\langle T_{\vec{n}} \rangle_{\vec{n}}$ does not vanish, but the correction terms are once again of fourth and higher order when the $V_{\vec{\alpha}}$ are independent random variables.

The criterion that the CP$\vec{n}$ be accurate is similar to that for the CPA. Equation (3.19a) implies that the addition of site $\vec{\alpha}$ to cluster $\vec{n}$ does not affect the self-energy on site $\beta \notin \vec{n}, \vec{\alpha}$. This requires that the effect of adding another atom to a cluster decay rapidly away from the cluster, i.e., that the coherence length be short. This in turn suggests that quantitatively accurate results can be obtained from the CP$\vec{n}$ for extended states when the cluster radius becomes larger than the mean free path. Since no difficulties exist in dealing with long mean free paths, fairly rapid convergence is expected whenever the CP$\vec{n}$ treatment is warranted, i.e., in strongly disordered systems with short mean free paths.

IV. PROPERTIES OF CP$\vec{n}$ APPROXIMATION

In this section, we assume that the CP$\vec{n}$ approximation (3.19) has been made for a particular cluster $\vec{n}$.

A. Self-Consistency

The proper self-energy is obtained in the CP$\vec{n}$ from Eqs. (3.19b) and (3.19c). We now prove that it satisfies the equation of motion, or rather its equivalent (2.15), once (3.19b) is substituted for $T^{\vec\alpha}_{\vec n}$ therein. We start by rewriting (3.19b) and then averaging it:

$$\langle T^{\vec\alpha}_{\vec n}\rangle^{\vec\alpha}\equiv\langle (V_{\vec\alpha}-\sigma^{(\alpha)}_{\vec n})(1+G_{\vec n}T^{\vec\alpha}_{\vec n})\rangle^{\vec\alpha}=0 \quad (\mathrm{CP}\vec{\mathrm{n}}) . \qquad (4.1)$$

This may be rewritten as

$$\sigma^{(\alpha)}_{\vec n}=\langle V_{\vec\alpha}+V_{\vec\alpha}G_{\vec n}T^{\vec\alpha}_{\vec n}\rangle^{\vec\alpha} - \sigma^{(\alpha)}_{\vec n}G_{\vec n}\langle T^{\vec\alpha}_{\vec n}\rangle^{\vec\alpha} \quad (\mathrm{CP}\vec{\mathrm{n}}) . \qquad (4.2)$$

As the last term in (4.2) vanishes according to (3.19c), it is identical to (2.15) as required.

We certainly do not expect the correct formal structure of the hierarchy to be preserved for $m>n$ once the CP$\vec{\mathrm{n}}$ is made. However, we can show that "self-consistency," i.e.,

$$\langle T^{\vec\alpha}_{\vec m}\rangle^{\vec\alpha}=0, \quad \text{all } \vec{\mathrm{m}}\subseteq\vec{\mathrm{n}}, \quad \alpha\notin\vec{\mathrm{m}} \qquad (4.3)$$

is preserved for all $\vec{\mathrm{m}}\subseteq\vec{\mathrm{n}}$, i.e., $0\leq m\leq n$. Before we can define the $T^{\vec\alpha}_{\vec m}$ which enters (4.3), we must introduce Green's functions $G_{\vec m}$ of order lower than the order $\vec{\mathrm{n}}$ for which the CP$\vec{\mathrm{n}}$ is carried out. This done by the general form of the exact consistency equation (2.19):

$$G_{\vec m}\equiv\langle G_{\vec n}\rangle^{\vec n-\vec m} \quad (\mathrm{CP}\vec{\mathrm{n}}) . \qquad (4.4)$$

We now prepare to obtain an equation of motion for $G_{\vec m}$ in the CP$\vec{\mathrm{n}}$ by rewriting the equation of motion of $G_{\vec n}$ [Eq. (2.11)] as

$$(E-H_0-V_{\vec m})G_{\vec n}-\sum_{\beta\in\vec n-\vec m}V_{\vec\beta}G_{\vec n}-\sum_{\alpha\notin\vec n}\langle V_{\vec\alpha}G_{\vec n,\vec\alpha}\rangle^{\vec\alpha}=1 . \qquad (4.5)$$

To make explicit the introduction of the CP$\vec{\mathrm{n}}$ [Eq. (3.19a)] into $G_{\vec n,\vec\alpha}$, we relabel it as

$$G_{\vec n,\vec\alpha}\Rightarrow G^{\vec\alpha}_{\vec n}=[E-H_0-V_{\vec n}-\sigma_{\vec n}-(V_{\vec\alpha}-\sigma^{(\alpha)}_{\vec n})]^{-1} \quad (\mathrm{CP}\vec{\mathrm{n}}) . \qquad (4.6)$$

We see that an equation of the exact form [Eq. (2.14)] holds for $G^{\vec\alpha}_{\vec n}$,

$$G^{\vec\alpha}_{\vec n}=G_{\vec n}+G_{\vec n}T^{\vec\alpha}_{\vec n}G_{\vec n} \quad (\mathrm{CP}\vec{\mathrm{n}}) , \qquad (4.7)$$

with $T^{\vec\alpha}_{\vec n}$ given by (3.19b) and $G_{\vec n}$ by (2.11) *in the* CP$\vec{\mathrm{n}}$. Multiplying by $V_{\vec\alpha}$, averaging over site α, and using (2.15) since, as shown by (4.2), it holds in the CP$\vec{\mathrm{n}}$, gives

$$\langle V_{\vec\alpha}G^{\vec\alpha}_{\vec n}\rangle^{\vec\alpha}=\sigma^{(\alpha)}_{\vec n}G_{\vec n} \quad (\mathrm{CP}\vec{\mathrm{n}}) , \qquad (4.8)$$

which is structurally of the form (2.13).

We can now average down the equation of motion (4.5) in accordance with (4.4) and get

$$(E-H_0-V_{\vec m})G_{\vec m}-\sum_{\beta\in\vec n-\vec m}\langle V_{\vec\beta}G_{\vec m,\vec\beta}\rangle^{\vec\beta} - \sum_{\alpha\notin\vec n}\langle V_{\vec\alpha}G^{\vec\alpha}_{\vec m}\rangle^{\vec\alpha}=1 \quad (\mathrm{CP}\vec{\mathrm{n}}), \qquad (4.9)$$

where

$$G^{\vec\alpha}_{\vec m}\equiv\langle G_{\vec n,\vec\alpha}\rangle^{\vec n-\vec m}\Rightarrow\langle G^{\vec\alpha}_{\vec n}\rangle^{\vec n-\vec m} \quad (\mathrm{CP}\vec{\mathrm{n}}) . \qquad (4.10)$$

At this point we can introduce lower-order T matrices through

$$G^{\vec\alpha}_{\vec m}\equiv G_{\vec m}+G_{\vec m}T^{\vec\alpha}_{\vec m}G_{\vec m}, \quad \alpha\notin\vec{\mathrm{n}} \quad (\mathrm{CP}\vec{\mathrm{n}}) \qquad (4.11\mathrm{a})$$

$$G_{\vec m,\vec\beta}\equiv G_{\vec m}+G_{\vec m}T^{\vec\beta}_{\vec m}G_{\vec m} , \quad \beta\in\vec{\mathrm{n}}-\vec{\mathrm{m}} \quad (\mathrm{CP}\vec{\mathrm{n}}) . \qquad (4.11\mathrm{b})$$

The equation of motion (4.9) and the T-matrix definitions (4.11) enable us to obtain explicit expressions for the self-energy $\sigma^{(\alpha)}_{\vec m}$ defined through

$$G_{\vec m}=\Bigl(E-H_0-V_{\vec m}-\sum_{\alpha\notin\vec m}\sigma^{(\alpha)}_{\vec m}\Bigr)^{-1} , \qquad (4.12)$$

namely,

$$\sigma^{(\alpha)}_{\vec m}=\langle V_{\vec\alpha}+V_{\vec\alpha}G_{\vec m}T^{\vec\alpha}_{\vec m}\rangle^{\vec\alpha}, \quad \text{all } \alpha\notin\vec{\mathrm{m}} \quad (\mathrm{CP}\vec{\mathrm{n}}) \qquad (4.13)$$

which has the same form as in the exact theory. Similarly, comparing (4.9) and (4.12) leads again to relations of the same form as in the exact theory:

$$\sigma^{(\alpha)}_{\vec m}G_{\vec m}=\langle V_{\vec\alpha}G_{\vec m,\vec\alpha}\rangle^{\vec\alpha}, \quad \alpha\in\vec{\mathrm{n}}-\vec{\mathrm{m}} \quad (\mathrm{CP}\vec{\mathrm{n}}) \qquad (4.14\mathrm{a})$$

$$\sigma^{(\alpha)}_{\vec m}G_{\vec m}=\langle V_{\vec\alpha}G^{\vec\alpha}_{\vec m}\rangle^{\vec\alpha}, \quad \alpha\notin\vec{\mathrm{n}} \quad (\mathrm{CP}\vec{\mathrm{n}}) . \qquad (4.14\mathrm{b})$$

Because $T^{\vec\alpha}_{\vec m}$ is defined as a scattering matrix through (4.11), it obeys the equation

$$T^{\vec\alpha}_{\vec m}G_{\vec m}=U^{\vec\alpha}_{\vec m}G_{\vec m,\vec\alpha}, \quad \alpha\in\vec{\mathrm{n}}-\vec{\mathrm{m}} \quad (\mathrm{CP}\vec{\mathrm{n}}) \qquad (4.15\mathrm{a})$$

$$T^{\vec\alpha}_{\vec m}G_{\vec m}=U^{\vec\alpha}_{\vec m}G^{\vec\alpha}_{\vec m}, \quad \alpha\notin\vec{\mathrm{n}} \quad (\mathrm{CP}\vec{\mathrm{n}}) . \qquad (4.15\mathrm{b})$$

From (2.18) and the definitions of the self-energies entering the Green's functions in (4.15), we have

$$U^{\vec\alpha}_{\vec m}=V_{\vec\alpha}-\sigma^{(\alpha)}_{\vec m}+\sum_{\beta\notin\vec m,\vec\alpha}(\sigma^{(\beta)}_{\vec m,\vec\alpha}-\sigma^{(\beta)}_{\vec m}), \quad \alpha\in\vec{\mathrm{n}}-\vec{\mathrm{m}} \quad (\mathrm{CP}\vec{\mathrm{n}}) \qquad (4.16\mathrm{a})$$

$$U^{\vec\alpha}_{\vec m}=V_{\vec\alpha}-\sigma^{(\alpha)}_{\vec m}+\sum_{\beta\notin\vec m/\vec\alpha}(\sigma^{\vec\alpha(\beta)}_{\vec m}-\sigma^{(\beta)}_{\vec m}), \quad \alpha\notin\vec{\mathrm{n}} \quad (\mathrm{CP}\vec{\mathrm{n}}) . \qquad (4.16\mathrm{b})$$

We have defined the self-energy $\sigma^{\vec\alpha(\beta)}_{\vec m}$ as follows:

$$\sigma^{\vec\alpha(\beta)}_{\vec m}G^{\vec\alpha}_{\vec m}=\langle\sigma^{(\beta)}_{\vec n}G^{\vec\alpha}_{\vec n}\rangle^{\vec n-\vec m}, \quad \beta\notin\vec{\mathrm{n}},\vec\alpha \quad (\mathrm{CP}\vec{\mathrm{n}}) \qquad (4.17\mathrm{a})$$

$$\sigma^{\vec\alpha(\beta)}_{\vec m}G^{\vec\alpha}_{\vec m}=\langle V_{\vec\beta}G^{\vec\alpha}_{\vec n}\rangle^{\vec n-\vec m}, \quad \beta\in\vec{\mathrm{n}}-\vec{\mathrm{m}} \quad (\mathrm{CP}\vec{\mathrm{n}}) . \qquad (4.17\mathrm{b})$$

This in turn enables us to make the definition

$$G^{\vec\alpha}_{\vec m}\equiv(E-H_0-V_{\vec m,\vec\alpha}-\sigma^{\vec\alpha}_{\vec m})^{-1}, \quad \alpha\notin\vec{\mathrm{n}} \quad (\mathrm{CP}\vec{\mathrm{n}}) \qquad (4.18\mathrm{a})$$

$$\sigma^{\vec\alpha}_{\vec m}=\sum_{\beta\quad\vec m,\vec\alpha}\sigma^{\vec\alpha(\beta)}_{\vec m} \quad (\mathrm{CP}\vec{\mathrm{n}}) . \qquad (4.18\mathrm{b})$$

Averaging (4.15) over site $\vec\alpha$ gives

$$\langle T^{\vec\alpha}_{\vec m}G_{\vec m}\rangle^{\vec\alpha}=\langle T^{\vec\alpha}_{\vec m}\rangle^{\vec\alpha}G_{\vec m}=\langle U^{\vec\alpha}_{\vec m}G_{\vec m,\vec\alpha}\rangle^{\vec\alpha}, \quad \alpha\in\vec{\mathrm{n}}-\vec{\mathrm{m}} \quad (\mathrm{CP}\vec{\mathrm{n}}) \qquad (4.19\mathrm{a})$$

$$\langle T^{\vec\alpha}_{\vec m}G_{\vec m}\rangle^{\vec\alpha}=\langle U^{\vec\alpha}_{\vec m}G^{\vec\alpha}_{\vec m}\rangle^{\vec\alpha} \quad \alpha\notin\vec{\mathrm{n}} \quad (\mathrm{CP}\vec{\mathrm{n}}) . \qquad (4.19\mathrm{b})$$

Upon substitution of (4.16) into (4.19), the terms containing $V_{\vec{\alpha}} - \sigma_{\vec{m}}^{(\alpha)}$ vanish because of (4.14) and (4.18), as does each of the terms in the sum over β. Equation (4.19) vanishes identically; therefore, the self-consistency condition (4.3) follows in the CP$\vec{n}$.

B. Locality of $\sigma_{\vec{n}}^{(\alpha)}$ in CP$\vec{n}$

One particularly simple model has been of great utility in the study of disordered crystalline alloys, e.g., within the CPA.[1] In that model, H_0 has the full translational symmetry of the crystal. The fluctuation potentials $V_{\vec{\alpha}}$ depend on the particular atom on a site and are independent random variables under the assumption of complete compositional disorder. Finally, it is supposed that only a single energy band is involved and the $V_{\vec{\alpha}}$ are local in the crystal coordinate, or Wannier, representation for that band:

$$(\beta|V_{\vec{\alpha}}|\gamma) = v_{\vec{\alpha}}\,\delta_{\beta\alpha}\,\delta_{\gamma\alpha}\ . \qquad (4.20a)$$

Here the $v_{\vec{\alpha}}$ are the amplitudes of the single-site potentials, they are random variables and are not necessarily restricted to only two possible variables. The Greek indices are here used to label sites of atomic occupancy. We now prove that $\sigma_{\vec{n}}^{(\alpha)}$ and $T_{\vec{n}}^{\vec{\alpha}}$ are similarly site diagonal.

Because $V_{\vec{\alpha}}$ occurs as the left-most factor in (2.15), (4.20) automatically implies that

$$(\beta|\sigma_{\vec{n}}^{(\alpha)}|\gamma) = \delta_{\alpha\beta}\,(\alpha|\sigma_{\vec{n}}^{(\alpha)}|\gamma)\ , \qquad (4.20b)$$

and similarly,

$$(\beta|\sigma_{\vec{m}}^{(\alpha)}|\gamma) = \delta_{\alpha\beta}\,(\alpha|\sigma_{\vec{m}}^{(\alpha)}|\gamma) \quad (\mathrm{CP}\vec{n}) \qquad (4.21)$$

from (4.13). In CP$\vec{n}$, Eqs. (3.19b), (4.6), and (4.7) permit us to write

$$G_{\vec{n}}\,T_{\vec{n}}^{\vec{\alpha}} = G_{\vec{n}}^{\vec{\alpha}}\,(V_{\vec{\alpha}} - \sigma_{\vec{n}}^{(\alpha)})\ . \qquad (4.22)$$

Substituting (4.22) into (2.15) gives

$$\begin{aligned}(\alpha|\sigma_{\vec{n}}^{(\alpha)}|\gamma) &= \langle v_{\vec{\alpha}} + v_{\vec{\alpha}}\,(\alpha|G_{\vec{n}}^{\vec{\alpha}}|\alpha)\,v_{\vec{\alpha}}\rangle^{\vec{\alpha}}\,\delta_{\gamma\alpha} \\ &\quad - \langle v_{\vec{\alpha}}\,(\alpha|G_{\vec{n}}^{\vec{\alpha}}|\alpha)\rangle^{\vec{\alpha}}\,(\alpha|\sigma_{\vec{n}}^{(\alpha)}|\gamma) \\ &= \frac{\langle v_{\vec{\alpha}} + v_{\vec{\alpha}}\,(\alpha|G_{\vec{n}}^{\vec{\alpha}}|\alpha)\,v_{\vec{\alpha}}\rangle^{\vec{\alpha}}}{1 + \langle v_{\vec{\alpha}}\,(\alpha|G_{\vec{n}}^{\vec{\alpha}}|\alpha)\rangle^{\vec{\alpha}}}\,\delta_{\gamma\alpha}\ , \end{aligned} \qquad (4.23)$$

so that $\sigma_{\vec{n}}^{(\alpha)}$ is site diagonal. With (4.23) established, (3.19b) shows immediately that $T_{\vec{n}}^{\vec{\alpha}}$ is similarly site diagonal.

Even though $\sigma_{\vec{n}}^{(\alpha)}$ is site diagonal, it is obviously not site independent. It does not exist for the sites $\in \vec{n}$ and, because the specifying of the cluster potential $V_{\vec{n}}$ destroys the translational invariance, it must depend on the position of α relative to the cluster. In order that CP$\vec{n}$ calculations be computationally feasible; it is necessary that the $\sigma_{\vec{n}}^{(\alpha)}$ are site dependent only within a finite region. This important property of CP$\vec{n}$ is proven in Sec. IV C.

The above proof of locality can be generalized to include localization of $V_{\vec{\alpha}}$ to any subset of sites. If $V_{\vec{\alpha}}$ is a matrix which has nonzero elements only for a set of r sites related to α so that it can be represented by an $r\times r$ submatrix, $\sigma_{\vec{n}}^{(\alpha)}$ and $T_{\vec{n}}^{(\alpha)}$ have similar $r\times r$ representations. This allows immediate generalization of the CPA and the higher CP$\vec{n}$ to include randomness in the off-diagonal elements of the Hamiltonian.[11,12]

C. Asymptotic Limits of $G_{\vec{m}}$, $\sigma_{\vec{m}}^{(\alpha)}$ in CP$\vec{n}$

Wave functions in a disordered system are either extended with a finite-phase coherence length (similar to a mean free path) or are localized; the Green's functions must have finite range. Ignoring the breakdown of translation invariance introduced by the fixed cluster potential permits us to represent this finite range schematically by

$$(\alpha|G_{\vec{n}}|\beta) \xrightarrow[R_{\alpha\beta}\to\infty]{} g_{\vec{n}}\,e^{-\kappa_{\vec{n}}R_{\alpha\beta}}/R_{\alpha\beta}\ , \qquad (4.24)$$

where $R_{\alpha\beta}$ is the distance between sites α and β, and $1/\kappa_{\vec{n}}$ is the coherence length. Since all lower-order Green's functions $G_{\vec{m}}$ may be obtained from $G_{\vec{n}}$ by averaging down over $\vec{n}-\vec{m}$, (4.24) implies that all lower $G_{\vec{m}}$ are of finite range, denoted schematically by

$$(\alpha|G_{\vec{m}}|\beta) \xrightarrow[R_{\alpha\beta}\to\infty]{} g_{\vec{m}}\,e^{-\kappa_{\vec{m}}R_{\alpha\beta}}/R_{\alpha\beta}, \qquad \vec{m}\subseteq\vec{n}\ . \qquad (4.25)$$

Thus, according to (4.24) and (4.25), information concerning the presence of the cluster must decay, at least as $e^{-\kappa R_{\alpha\gamma}}/R_{\alpha\gamma}$ for quantities such as $G_{\vec{n}}^{\vec{\alpha}}$, $T_{\vec{n}}^{\vec{\alpha}}$, and $\sigma_{\vec{n}}^{(\alpha)}$, where γ is a site in the cluster $\vec{n}$ and α is far away. This suggests particularly simple asymptotic limits, which we now proceed to explore. In particular, it is possible that all quantities become independent of the presence of the cluster $\vec{n}$, asymptotically.

Let us suppose that such an asymptotic region exists and examine the consequences of our assumption:

$$\sigma_{\vec{n}}^{(\alpha)} \xrightarrow[R_{\alpha\gamma}\to\infty]{} \sigma_A^{(\alpha)}\ , \qquad (4.26a)$$

where $\sigma_A^{(\alpha)}$ is α independent up to a translation, and hence

$$(\alpha|G_{\vec{n}}|\beta) \to (\alpha|G_A|\beta), \quad R_{\alpha\gamma} \text{ or } R_{\beta\gamma}\to\infty \qquad (4.26b)$$

where G_A is translationly invariant and of finite range. Let us write G_A in the general form

$$G_A = (E - H_0 - \textstyle\sum_\alpha W_A^{(\alpha)})^{-1}\ , \qquad (4.27)$$

where the $W_A^{(\alpha)}$ are invariant up to a translation. We may define a T matrix as follows:

$$G_{\vec{n}} = G_A + G_A\,T_{\vec{n}A}\,G_A\ , \qquad (4.28a)$$

$$T_{\vec{n}A} = U_{\vec{n}A}\,(1 - G_A\,U_{\vec{n}A})^{-1}\ , \qquad (4.28b)$$

$$U_{\vec{n}A}=\sum_{\alpha} U_{\vec{n}A}^{\vec{\alpha}}=\sum_{\alpha\in\vec{n}}\left(V_{\vec{\alpha}}-W_A^{(\alpha)}\right)+\sum_{\alpha\notin\vec{n}}\left(\sigma_{\vec{n}}^{(\alpha)}-W_A^{(\alpha)}\right) . \tag{4.28c}$$

Now $G_{\vec{n}}$ must equal G_A asymptotically. Since G_A has finite range, this requires finite range and localization of $T_{\vec{n}A}$, according to (4.28a). Finite range and localization for $T_{\vec{n}A}$ results only from finite range and localization for $U_{\vec{n}A}$, according to (4.28b). Equation (4.28c) guarantees a local $U_{\vec{n}A}$ only if

$$\sigma_{\vec{n}}^{(\alpha)} \xrightarrow[R_{\alpha\gamma}\to\infty]{} W_A^{(\alpha)} , \tag{4.29}$$

which implies that

$$W_A^{(\alpha)}=\sigma_A^{(\alpha)} . \tag{4.30}$$

We note for clarity that by finite range we mean that a matrix $(\alpha|M|\beta)\to 0$ as $R_{\alpha\beta}\to\infty$, and by local we mean that

$$(\alpha|M_{\vec{n}}|\beta)\to 0 \quad \text{as} \quad R_{\alpha\gamma} \quad \text{or} \quad R_{\beta\gamma}\to\infty .$$

Turning now to the CP$\vec{n}$, the self-consistency requirement (4.23) gives $\sigma_A^{(\alpha)}$ site diagonal with amplitude

$$\sigma_A^{(\alpha)}=\frac{\langle v_{\vec{\alpha}}+v_{\vec{\alpha}}\,(\alpha|G_A^{\vec{\alpha}}|\alpha)\,v_{\vec{\alpha}}\rangle^{\vec{\alpha}}}{1+\langle v_{\vec{\alpha}}\,(\alpha|G_A^{\vec{\alpha}}|\alpha)\rangle^{\vec{\alpha}}} \quad (\text{CP}\vec{n}) , \tag{4.31}$$

where $G_A^{\vec{\alpha}}$ is the asymptotic limit of $G_{\vec{n}}^{\vec{\alpha}}$, Eq. (4.6),

$$G_A^{\vec{\alpha}}=[E-H_0-\sigma_{\vec{A}}-(V_{\vec{\alpha}}-\sigma_A^{(\alpha)})]^{-1} \quad (\text{CP}\vec{n}) \tag{4.32}$$

and

$$\sigma_{\vec{A}}=\textstyle\sum_{\alpha}\sigma_A^{(\alpha)} \quad (\text{CP}\vec{n}) . \tag{4.33}$$

Equation (4.31) may be rewritten immediately as

$$\sigma_A^{(\alpha)}=\langle V_{\vec{\alpha}}+V_{\vec{\alpha}}\,G_A\,T_A^{\vec{\alpha}}\rangle^{\vec{\alpha}} \quad (\text{CP}\vec{n}) , \tag{4.34a}$$

where

$$T_A^{\vec{\alpha}}=(V_{\vec{\alpha}}-\sigma_A^{(\alpha)})[1-G_A(V_{\vec{\alpha}}-\sigma_A^{(\alpha)})]^{-1} \quad (\text{CP}\vec{n}) \tag{4.34b}$$

and

$$\langle T_A^{\vec{\alpha}}\rangle^{\vec{\alpha}}=0 \quad (\text{CP}\vec{n}) . \tag{4.34c}$$

Equation (4.34) is identical in structure to the defining equations of the CPA (≡CP$\vec{0}$), (3.7) and (3.8). Thus, we have shown that if the Green's functions are assumed to have finite range and if translation-invariant asymptotic forms are assumed for all quantities, the CP$\vec{n}$ reduces to the CPA asymptotically.

We now quote a result relating the relative rates at which $G_{\vec{n}}$ and $\sigma_{\vec{n}}^{(\alpha)}$ approach their asymptotic limits. Let

$$\sigma_{\vec{n}}^{(\alpha)} \xrightarrow[R_{\alpha\gamma}\to\infty]{} \sigma_A^{(\alpha)}+s_A(R_{\alpha\gamma}), \quad \gamma\in\vec{n} \tag{4.35a}$$

$$(\alpha|G_{\vec{n}}|\alpha) \xrightarrow[R_{\alpha\gamma}\to\infty]{} (\alpha|G_A|\alpha)+g_A(R_{\alpha\gamma}) \tag{4.35b}$$

be the definitions of s_A and g_A, which are taken as small. We have shown that

$$s_A\approx O(g_A{}^2) \quad (\text{CP}\vec{n}) \tag{4.36}$$

by a detailed analysis of the corresponding generalizations of (4.34). In other words, $\sigma_{\vec{n}}^{(\alpha)}$ approaches asymptotic behavior faster than $G_{\vec{n}}$.

The fact that the CPA $\sigma_A^{(\alpha)}$ is the asymptotic limit of the CP$\vec{n}$ $\sigma_{\vec{n}}^{(\alpha)}$ is important in any calculations involving CP$\vec{n}$. Thus, the CP$\vec{n}$ equations (3.19) could be solved self-consistently by initially using $\sigma_A^{(\alpha)}$ for $\sigma_{\vec{n}}^{(\alpha)}$ and then iterating. The first step is merely a Koster-Slater impurity problem for the cluster $\vec{n}$ in the CPA environment. Preliminary calculations of this nature have been carried out by Kirkpatrick in these laboratories. Since these calculations have direct bearing on the existence of localized states in the band tails, the above iteration scheme is discussed in Sec. VII. Alternatively, inside of the CPA band, $\sigma_{\vec{n}}^{(\alpha)}$ can be expanded directly in a power series of CPA quantities. This expansion, which is discussed in Sec. V C, could be used to improve convergence.

Because the $G_{\vec{m}}$, $\vec{m}\subseteq\vec{n}$, are obtained from $G_{\vec{n}}$ by averaging down over $\vec{n}-\vec{m}$ in the CP$\vec{n}$, precisely the same asymptotic behavior holds for all $\vec{m}\subset\vec{n}$ and, in particular for G_0. Clearly, at this stage of development of the theory, no essential improvement over the CPA is achieved by fixing the potential associated with a localized cluster except in the vicinity of that cluster. This, as we shall see, allows for certain of the localized states, but the CP$\vec{n}$ must be augmented before it yields a significant improvement over CPA throughout the material.

V. AVERAGE GREEN'S FUNCTION: ECP$\vec{n}$

The physical quantity of interest is the average Green's function $\langle \mathcal{G}\rangle=G_0$. An approximation to G_0 is obtained directly by stopping the CP$\vec{n}$ at level $\vec{0}$, i.e., by using the CPA. It was argued in Sec. III B, however, that the higher n, the more accurate the CP$\vec{n}$ can be expected to be, at least within the cluster. We therefore used a prescription for calculating a lower-order Green's function $G_{\vec{m}}^{(\vec{n})}$, $\vec{m}\subset\vec{n}$, ($G_0^{(\vec{n})}$ in particular) from a $G_{\vec{n}}$ obtained via the CP$\vec{n}$. The simplest prescription involves only averaging down, i.e.,

$$G_{\vec{m}}^{(\vec{n})}=\langle G_{\vec{n}}\rangle^{\vec{n}-\vec{m}}, \quad G_0^{(\vec{n})}=\langle G_{\vec{n}}\rangle^{\vec{n}} \quad (\text{CP}\vec{n}) , \tag{5.1}$$

which is discussed in detail in Sec. IV A. However, the CP$\vec{n}$ singles out a particular set of atoms or sites $\vec{n}$ through the approximation on $\sigma_{\vec{n},\vec{\alpha}}^{(\beta)}$, all $\beta\notin\vec{n},\vec{\alpha}$ and all $\vec{\alpha}\notin\vec{n}$, Eq. (3.19a). The use of the CP$\vec{n}$ in (5.1) does not yield a translationally invariant approximation to G_0 as is required. The cluster $\vec{n}$ could have been taken anywhere so that averaging $G_0^{(\vec{n})}$ over all clusters translationally equivalent to the original one restores its translational invariance. Next, there is nothing special about any particular cluster configuration for fixed n, so that $G_0^{(\vec{n})}$ should be averaged in addition over all cluster configurations of n atoms in which the relative separations of the atoms or sites are sufficiently small that the cluster does not decompose into two independent parts. We would then have

$$G_0^{(\vec{n})\prime} = \sum_{\vec{n}} P_{\vec{n}} G_0^{(\vec{n})} \quad (\mathrm{CP}\vec{n}) \tag{5.2}$$

for the averaged Green's function, where the summation is over all clusters of order n as stated above. In (5.2), $P_{\vec{n}}$ is the probability of a given cluster $\vec{n}$ in an ensemble of all possible configurations.

To examine how $G_0^{(n)\prime}$ differs from the CPA result, we deal explicitly with the case $n=1$. We have from (5.2)

$$G_0^{(1)\prime} = \sum_\alpha p_{\vec{\alpha}} \langle G_{\vec{\alpha}} \rangle^{\vec{\alpha}} = (1/N) \sum_\alpha \langle G_{\vec{\alpha}} \rangle^{\vec{\alpha}} \quad (\mathrm{CP1}), \tag{5.3}$$

since $p_{\vec{\alpha}}$ is the probability for specifying one site out of a total of N sites or $1/N$. Taking matrix elements, we get

$$(\beta | G_0^{(1)\prime} | \gamma) = (\beta | G_A | \gamma) + (1/N) \times \sum_\alpha [(\beta | \langle G_{\vec{\alpha}} \rangle^{\vec{\alpha}} | \gamma) - (\beta | G_A | \gamma)] \quad (\mathrm{CP1}), \tag{5.4}$$

where

$$(\beta | \langle G_{\vec{\alpha}} \rangle^{\vec{\alpha}} | \gamma) \xrightarrow[R_{\beta\alpha} \text{ or } R_{\gamma\alpha} \to \infty]{} (\beta | G_A | \gamma) \quad (\mathrm{CP1}) . \tag{5.5}$$

The asymptotic Green's function G_A is just the CPA result according to Sec. IV C. Let R_0 be the distance beyond which asymptotic behavior is manifested. We obtain from (5.4) that

$$(\beta | \Delta G | \gamma) \sim O[\mathfrak{N}(\beta, \gamma; R_0)/N] (\beta | G_A | \gamma) \quad (\mathrm{CP1}), \tag{5.6}$$

where ΔG is $G_0^{(1)\prime} - G_A$ and $\mathfrak{N}(\beta, \gamma; R_0)$ is the number of sites satisfying $R_{\beta\alpha}$ or $R_{\gamma\alpha} < R_0$. Thus $\Delta G \to 0$ and $G_0^{(1)\prime} \to G_A$ as N increases to infinity. In other words, no calculation of G_0 based on a translationally invariant form of the simple CP$\vec{n}$ can yield a result different from CPA if n remains finite as N goes to infinity. We require therefore for nontrivial results a subtle generalization of the averaging process used thus far. In Sec. V, we develop such a generalization and examine its properties. In Sec. VI, an alternate approach which results directly from the cluster hierarchy is discussed.

A. Final Averaging

It is clear from the above arguments that in order to obtain a $G_0^{(n)\prime}$ which is different from the CPA it is necessary to allow for the possibility of having specified clusters everywhere densely distributed throughout space. The total size of the specified cluster divided by N then remains finite when $N \to \infty$. Since it is impossible, practically as well as formally, to do CP$\vec{n}$ in the limit $n \to \infty$ in the general case, we must consider only certain special cases. For a single compact cluster $\vec{n}$, it is expected that $G_0^{(\vec{n})}$ provides an improvement over the CPA in the region of the cluster $\vec{n}$, an assertion which is amplified in Sec. VII where localized states are discussed. Thus, the CP$\vec{n}$ $G_0^{(\vec{n})}$ has nontrivial, but finite, information content above that contained in the CPA $G_0^{(0)}$. However, this information content was lost in (5.4) because it was spread out uniformly over infinite space. We now show how the information content of $G_0^{(\vec{n})}$ can be made macroscopic in the sense that the improved approximation to G_0, say $G_0^{(n)}$, which is solely determined by the $G_0^{(\vec{n})}$, differs from $G_0^{(0)}$ in a totally nontrivial manner.

First, it is convenient to consider the case of a single cluster $\vec{n}$ in CP$\vec{n}$, where $\vec{n}$ is divided into two disjoint subclusters $\vec{l}$ and $\vec{m}$. If we take $\vec{l}$ and $\vec{m}$ each to be compact, then

$$G_{\vec{n}} \equiv G_{\vec{l},\vec{m}} \tag{5.7}$$

has the asymptotic properties of CP$\vec{n}$ as given in Sec. IV C. The presence of the specified clusters $\vec{l}$ and $\vec{m}$ imply a local nonzero value of $U_{\vec{l},\vec{m}A}$ of (4.28c) and (4.30) in the region around the clusters $\vec{l}$ and $\vec{m}$,

$$(\alpha | U_{\vec{l},\vec{m}A} | \alpha) \neq 0, \quad R_{\alpha\gamma} < R_1, \quad \gamma \in \vec{l} \text{ or } \vec{m} \tag{5.8}$$

where R_1 measures the range over which the self-energy $\sigma_{\vec{l},\vec{m}}^{(\alpha)}$ differs from the CPA. By (4.35) and (4.36), $R_1 < R_0$, where R_0 is the range used in (5.6). For $R_{\lambda\mu} > 2R_0$, $\lambda \in \vec{l}$ and $\mu \in \vec{m}$, the $\sigma_{\vec{l},\vec{m}}^{(\alpha)}$ just differs from $\sigma_A^{(\alpha)}$ only in the two disjoint regions $R_{\alpha\lambda}$ and $R_{\alpha\mu} < R_1$ about the subclusters $\vec{l}$ and m. Specifically,

$$G_{\vec{l},\vec{m}} = G_{\vec{l}} + G_{\vec{l}} \sum_{\alpha, R_{\alpha\mu} < R_1} U_{\vec{l},\vec{m}}^{(\vec{\alpha})} G_{\vec{l},\vec{m}} \quad (\mathrm{CP}\vec{n}), \tag{5.9}$$

where $U_{\vec{l},\vec{m}}^{(\vec{\alpha})}$ is defined as usual by (5.9), so that upon taking matrix elements

$$(\beta | G_{\vec{l},\vec{m}} | \gamma) = (\beta | G_{\vec{l}} | \gamma) + \sum_{\alpha, R_{\alpha\mu} < R_1} (\beta | G_{\vec{l}} | \alpha)(\alpha | U_{\vec{l},\vec{m}}^{(\vec{\alpha})} | \alpha)(\alpha | G_{\vec{l},\vec{m}} | \gamma) \xrightarrow[R_{\beta\mu} \text{ or } R_{\gamma\mu} > R_0]{} (\beta | G_{\vec{l}} | \gamma) \quad (\mathrm{CP}\vec{n}) . \tag{5.10}$$

In particular, for $R_{\beta\lambda}$, $R_{\gamma\lambda} < R_0$, and therefore $R_{\mu\lambda} > 2R_0$, (5.10) gives

$$(\beta | G_{\vec{l},\vec{m}} | \gamma) = (\beta | G_{\vec{l}} | \gamma), \quad R_{\beta\lambda}, \; R_{\gamma\lambda} < R_0, \quad R_{\lambda\mu} > 2R_0 . \tag{5.11}$$

Thus, in the neighborhood of the subcluster $\vec{l}$, $G_{\vec{l},\vec{m}} \to G_{\vec{l}}$ which must just be the CP$\vec{l}$ result since $\vec{l}$ and $\vec{m}$ are beyond each other's range of influence.

Therefore, given the CP$\vec{n}$ $G_0^{(\vec{n})}$ for all $\vec{n}$, we automatically have the $G_0^{(\vec{n}_1,\vec{n}_2)}$ for $R_{\vec{n}_1\vec{n}_2} > 2R_0$, and hence $G_0^{(\vec{n}_1,\vec{n}_2,\cdots,\vec{n}_j,\cdots)}$, provided $R_{\vec{n}_i,\vec{n}_j} > 2R_0$ for all i and j, where $\vec{n}_i$ and $\vec{n}_j$ represent arbitrary clusters of size n. $G_0^{(\vec{n}_1,\vec{n}_2,\ldots,\vec{n}_j,\cdots)}$ therefore has specified information about clusters distributed densely throughout space, so that a final averaging which leads to a translationally invariant approximation to G_0 does not reduce to the CPA as in (5.2). It now remains to specify the optimum distribution of the clusters $\vec{n}_1, \vec{n}_2, \ldots, \vec{n}_j, \ldots$ in space and the nature of the final averaging to provide translational invariance. First, we require the clusters $\{\vec{n}_i\}$ to be as compact as possible to minimize $\max(\alpha_i, \beta_i \in \vec{n}_i) R_{\alpha_i\beta_i}$. Second, we want to obtain the maximum amount of information content in $G_0^{(\{\vec{n}_i\})}$ which is related to

$$W = \lim(1/N) \textstyle\sum_i \mathfrak{N}(\alpha_i, \beta_i; R_0) \quad \text{as } N \to \infty\,. \quad (5.12\text{a})$$

This is, of course, accomplished by choosing $\min(\alpha_i \in \vec{n}_i,\ \beta_j \in \vec{n}_j)\ R_{\alpha_i\beta_j} = 2R_0$ to allow the clusters to be as close as possible to each other. Thus, specifying $\vec{n}_1$ establishes a cell of size R_0 about $\vec{n}_1$, and $\vec{n}_2$ is then placed in a neighboring cell of size R_0, etc., until space has been filled. If $N(R_0)$ is the number of sites in such a cell, the total and optimal number of cells is $N/N(R_0)$. Since any cluster $\vec{n}_i$ could be centered in the ith cell, we must first average over the composition and type of cluster $\vec{n}_i$, provided it is kept centered in the ith cell so that its range of influence does not extend into neighboring cells. Thus, we have the extended CP$\vec{n}$ approximation (ECP$\vec{n}$)

$$G_0^{(\{n_i\})\prime} = \sum_{\{n_i\}} \left(\prod_i P_{\vec{n}_i}\right) G_0^{(\{\vec{n}_i\})} \quad (\text{E}'\text{CP}\vec{n})\,, \quad (5.12\text{b})$$

analogous to (5.2). Finally, the translational invariance must be restored; however, in (5.12b) after averaging over $\vec{n}_1$ in the center of each of the cells, all of the cells are equivalent, so that a translational-invariant averaging implies only a spatial averaging over all translationally equivalent sites within a single cell subject to cyclic boundary conditions. Thus, we first average over the compositions and the shape of $\vec{n}_i$ in the center of cluster i. Then cyclic boundary conditions are applied to the ith cell, and finally a translational average inside this ith cell is performed with these cyclic boundary conditions, i.e., we average over all possible positions of the cell origin subject to the usual cyclic boundary conditions.

Kohn[13] has also utilized a similar but less complete notion of periodically repeating a particular disordered configuration of limited spatial extent. Thus, if

$$G_0^{(n_i)} = \sum_{\vec{n}_i \in i} P_{\vec{n}_i} G_0^{(\vec{n}_i)\prime} \quad (\text{CP}\vec{n}\text{i}) \quad (5.13)$$

is a compositionally averaged Green's function, where $\sum'_{\vec{n}_i \in i}$ implies that the clusters $\vec{n}_i$ are "centered" in i as discussed above then let $G_{0i}^{(n)}$ be that part of $G_0^{(n_i)}$ in cell i, so that the translational average of $G_{0i}^{(n)}$ subject to cyclic boundary conditions is

$$\langle G_0^{(ni)} \rangle^{-1} = E - H_0 - \sum_{\alpha \in i} \sigma^{(\alpha)} \quad \text{in } i \ (\text{CP}\vec{n}\text{i}) \quad (5.14)$$

and, finally,

$$G_0^{(n)} = (E - H_0 - \textstyle\sum_\alpha \sigma^{(\alpha)})^{-1} \quad (\text{ECP}\vec{n}) \quad (5.15)$$

by the equivalence of averaged cells.

From the discussion in Sec. IV C, it is clear that the asymptoptic nature of CP$\vec{n}$ is related to the finite range of G_A. Thus, R_0 must be the order of magnitude of the coherence range $R_c = \max R_{\alpha\beta}$ for which $(\alpha | G_A | \beta) \neq 0$. (See Sec. V B for a more explicit discussion.) The latter is of the same order as the mean free path l for the CPA, and therefore the approximate magnitude of R_0 can be obtained directly from the CPA from the exponential decay of the off-diagonal elements of G_A as in (4.24) for G_A and $R_0 \equiv 1/\kappa_A$. It should be noted, however, that as the energy approaches the band edges, $l \to \infty$ and the above prescription would require that $R_0 \to \infty$. We would there be dealing with infinite compact clusters $\{\vec{n}_i\}$. The region near the band edges is thus inaccessible to our present theory. However, since bound states are described approximately in the theory (see Sec. VII), we can use it as a means of interpolating between the main body of the band, when it can be expected to hold, and the tails, where it is qualitatively correct, through the difficult transition region. The theory can be expected to be most accurate as W of (5.12a) approaches unity, i.e., when the radius of the largest compact cluster which can be treated is of order the mean free path or greater. We note that the case $l \to \infty$ is reminiscent of regions near critical points where infinite-range correlations, fluctuations, etc., must be included in any proper theory.

B. $\vec{k}$ Dependence of σ

Because of the lack of translational invariance of $G_0^{(\vec{n}_i)}$, it is clear that the self-energy associated with $G_0^{(n_i)}$ within cell i is not site diagonal. Therefore, the $\sigma^{(\alpha)}$ in (5.14) and (5.15) are no longer site diagonal at α, so the complete proper self-energy $\sigma_{\text{ECP}\vec{n}} = \sum_\alpha \sigma^{(\alpha)}$ is now $\vec{k}$ dependent, thereby introducing an improvement over the $\vec{k}$-independent $\sigma_0^{\vec{}}$ in CPA.

C. Corrections to CPA and ECP$\vec{n}$

Inside the CPA band, because of the finite density of states for the CPA, we can make a formal power-series expansion of the CP$\vec{n}$ $G_{\vec{n}}^{\alpha}$ of (4.6) in terms of the CPA G_A^α of (4.32):

$$G_{\vec{n}}^{\vec{\alpha}} = G_A^{\vec{\alpha}} + \lambda\, G_A^{\vec{\alpha}}\, U_{\vec{n}A}(\alpha)\, G_A^{\vec{\alpha}} + \cdots\,, \quad (5.16)$$

where λ is the formal expansion parameter and

$$U_{\vec{n}A}(\alpha) = U_{\vec{n}A} + \sigma_A^{(\alpha)} - \sigma_{\vec{n}}^{(\alpha)} \qquad (5.16')$$

by (4.28c) and (4.30). Substituting (5.16) into the self-consistency equation (4.23) for $\sigma_{\vec{n}}^{(\alpha)}$ and using the CPA result (4.31) gives a power-series expansion of $\sigma_{\vec{n}}^{(\alpha)}$ in terms of the CPA ,

$$\sigma_{\vec{n}}^{(\alpha)} = \sum_{j=0}^{\infty} \sigma_{\vec{n}}^{(\alpha;j)} \lambda^j , \qquad (5.17a)$$

where

$$\sigma_{\vec{n}}^{(\alpha;0)} = \sigma_A^{(\alpha)} , \qquad (5.17b)$$

$$\sigma_{\vec{n}}^{(\alpha;1)} = \sum_{\beta \in \vec{n}} \frac{\langle v_{\vec{\alpha}} \,|\, (\alpha | G_A^{\vec{\alpha}} | \beta)|^2 (v_{\vec{\alpha}} - \sigma_A^{(\alpha)})\rangle^{\vec{\alpha}} (v_{\vec{\beta}} - \sigma_A^{(\beta)})}{1 + \sigma_A^{(\alpha)} (\alpha | G_A | \alpha)} \qquad (5.17c)$$

is the magnitude of the first-order correction, while

$$\sigma_{\vec{n}}^{(\alpha;2)} = \Bigg(\sum_{\beta, \vec{\gamma}\ \vec{n}} \langle v_{\vec{\alpha}} (\alpha | G_A^{\vec{\alpha}} | \beta)(\beta | G_A^{\vec{\alpha}} | \gamma)(\gamma | G_A^{\vec{\alpha}} | \alpha)(v_{\vec{\alpha}} - \sigma_A^{(\alpha)})\rangle^{\vec{\alpha}} (v_{\vec{\beta}} - \sigma_A^{(\beta)})(v_{\vec{\gamma}} - \sigma_A^{(\gamma)})$$
$$+ \sum_{\beta \notin \vec{n}, \vec{\alpha}} \langle v_{\vec{\alpha}} \,|\, (\alpha | G_A^{\vec{\alpha}} | \beta)|^2 \ (v_{\vec{\alpha}} - \sigma_A^{(\alpha)})\rangle^{\vec{\alpha}} \sigma_{\vec{n}}^{(\beta;1)} - \sigma_{\vec{n}}^{(\alpha;1)} \sum_{\beta \in \vec{n}} \langle v_{\vec{\alpha}} (\alpha | G_A^{\vec{\alpha}} | \beta)\rangle^{\vec{\alpha}} (v_{\vec{\beta}} - \sigma_A^{(\beta)}) \Bigg) \, [1 + \sigma_A^{(\alpha)} (\alpha | G_A | \alpha)]^{-1} , \qquad (5.17d)$$

is that of the second-order correction, etc. Because of the finite coherence length in the CPA band,

$$(\alpha | G_A^{\vec{\alpha}} | \beta) \xrightarrow[R_{\alpha\beta} \to \infty]{} g_A \, e^{-\kappa_A R_{\alpha\beta}} / R_{\alpha\beta} , \qquad (5.18)$$

so that

$$\sigma_{\vec{n}}^{(\alpha;1)} \xrightarrow[R_{\alpha\beta} \to \infty]{} s_{\vec{n}A}^{(1)} e^{-2\kappa_A R_{\alpha\beta})} / R_{\alpha\beta}^2 , \quad \beta \in \vec{n} \qquad (5.19a)$$

$$\sigma_{\vec{n}}^{(\alpha;2)} \xrightarrow[R_{\alpha\beta} \to \infty]{} O(\sigma_{\vec{n}}^{(\alpha;1)}) + s_{\vec{n}A}^{(2)} e^{(-3\kappa_A R_{\alpha\beta})} / R_{\alpha\beta}^3 , \quad \beta \in \vec{n} \qquad (5.19b)$$

etc., which is merely a reflection of (4.35) and (4.36). Convergence of the expansion (5.17a) inside the CPA band thereby implies that the asymptotic range R_0 of CP$\vec{n}$ be of the order of the coherence range of the CPA. The use of (5.17) might therefore be a useful computational aid, given the CPA.

We can also examine the lowest-order corrections to CP$\vec{n}$ to give an indication as to the expected convergence properties of the ECP$\vec{n}$ approximation (see also Sec. VI). The examination of the lowest-order corrections in CP$\vec{n}$ proceeds directly as in CPA. Using the alternate definition of CP$\vec{n}$ embodied in (3.22) and (3.23), and assuming that the $V_{\vec{\alpha}}$ are independent variables, the lowest-order correction to $(\gamma | G_{\vec{n}}^{(\vec{n})} | \gamma')$ is the fourth-order contribution

$$\sum_{\alpha \neq \beta\ \alpha, \beta \notin \vec{n}} (\gamma | G_{\vec{n}} | \alpha) \, | (\alpha | G_{\vec{n}} | \beta)|^2 \ (\alpha | G_{\vec{n}} | \beta)(\beta | G_{\vec{n}} | \gamma')$$
$$\times \langle (T_{\vec{n}}^{\vec{\alpha}})^2 \rangle^{\vec{\alpha}} \langle (T_{\vec{n}}^{\vec{\beta}})^2 \rangle^{\vec{\beta}} , \qquad (5.20)$$

where all higher-order terms which involve only two-site scattering can easily be incorporated, as is done by Soven (see also Sec. VI). Because of the finite coherence range of $G_{\vec{n}}$ (4.24), the only contributions to (5.20) occur in the region $R_{\alpha\beta}$, $R_{\xi\zeta} < 1/\kappa_{\vec{n}}$, where $\xi = \gamma$, γ', $\zeta = \alpha$, β. The maximum terms in the summation occur for $\alpha\beta \in \gamma\gamma'$, but even for such terms the argument of the summand is still complex in the region of nonzero density of states because it contains the quantities $\langle (T_{\vec{n}}^{\vec{\alpha}})^2 \rangle^{\vec{\alpha}}$ (and $\vec{\alpha} \leftrightarrow \vec{\beta}$) and $(\alpha | G_{\vec{n}} | \beta)$ (and $\alpha \leftrightarrow \beta$). For large enough clusters $\vec{n}$, the summation runs over a number of terms with essentially random phases, and therefore is usually expected to be small. Near the band edges, Eq. (5.20) should be an extremely useful and delicate test of convergence.

Far enough from the cluster $\vec{n}$, when γ, γ', and all significant α, β are in the asymptotic region, Eq. (5.20) gives

$$\sum_{\alpha \neq \beta\ \alpha, \beta \notin \vec{n}} (\gamma | G_A | \alpha) \, | (\alpha | G_A | \beta)|^2 \langle (T_A^{\vec{\alpha}})^2 \rangle^{\vec{\alpha}} \langle (T_A^{\vec{\beta}})^2 \rangle^{\vec{\beta}}$$
$$\times (\alpha | G_A | \beta)(\beta | G_A | \gamma') , \qquad (5.21)$$

etc., for higher-order two-site scattering terms, thereby giving contributions which are independent of $\vec{n}$.

VI. AVERAGING VIA EQUATIONS OF MOTION: MULTIPLE-SCATTERING THEORY

In Sec. V, we obtained an approximate G_0 from CP$\vec{n}$ by averaging $G_{\vec{n}}$ and using the asymptotic properties of CP$\vec{n}$ to provide a translationally invariant result, the ECP$\vec{n}$ for G_0. This approach requires the evaluation of $G_{\vec{n}}$ for some set of suitably chosen compact clusters $\vec{n}$. There is, however, an alternate manner of utilization of the information contained in $\{G_{\vec{n}}$, CP$\vec{n}$, all $\vec{n}\}$ to produce a translationally invariant approximation to G_0.

This alternate approach of averaging can be used in conjunction with the CP$\vec{n}$ to provide recently sought generalizations of the CPA. This averaging procedure can also be used to provide a formal general solution to the hierarchy which should prove to be quite useful. As this method produces a theory which is more complicated than the CP$\vec{n}$, only the general formal development is presented here. Clearly, a more thorough discussion is merited; however, such a treatment is beyond the scope of the present work which places emphasis on the localized states in the band tails and the accompanying improvements over CPA. Rather than presenting the most general form of the formal solution to the hierarchy, the simplest solution is first obtained, then the generalizations and their properties are briefly discussed.

Assume that we are given a complete set of $G_{\vec{n}}^{(\vec{n})}$ in CP$\vec{n}$ for all $\vec{n}$. Then from the equation of motion for all possible $G_{\vec{n}-1}$ from (2.10),

$$(E-H_0-V_{\vec{n}-\vec{1}})\,G_{\vec{n}-\vec{1}}^{(nh)}-\sum_{\alpha\notin\vec{n}-\vec{1}}\langle V_{\vec{\alpha}}\,G_{\vec{n}-\vec{1},\vec{\alpha}}^{(\vec{n}-\vec{1},\vec{\alpha})}\rangle^{\vec{\alpha}}=1\,, \qquad (6.1)$$

where the superscript $(\vec{n})$ implies that a quantity is obtained directly from CP$\vec{n}$ and the superscript (nh) implies that it is obtained from the CP$\vec{n}$ via the hierarchy. Note that the terms in $\langle V_{\vec{\alpha}}G_{\vec{n}-\vec{1},\vec{\alpha}}^{(\vec{n}-\vec{1},\vec{\alpha})}\rangle^{\vec{\alpha}}$ are of finite range because of the finite coherence lenght of $G_{\vec{n}}$ and the presence of $V_{\vec{\alpha}}$ on the left. Since these terms in $\langle V_{\vec{\alpha}}\cdots\rangle^{\vec{\alpha}}$ are given by the CP$\vec{n}$, (6.1) is an inhomogeneous equation for $G_{\vec{n}-\vec{1}}^{(nh)}$ for all $\vec{n}-\vec{1}$. The solution is, therefore,

$$G_{\vec{n}-\vec{1}}^{(nh)}=g_{\vec{n}-\vec{1}}+g_{\vec{n}-\vec{1}}\sum_{\alpha\notin\vec{n}-\vec{1}}\langle V_{\vec{\alpha}}G_{\vec{n}-\vec{1},\vec{\alpha}}^{(\vec{n}-\vec{1},\vec{\alpha})}\rangle^{\vec{\alpha}}\,, \qquad (6.2)$$

where

$$g_{\vec{n}-\vec{1}}=(E-H_0-V_{\vec{n}-\vec{1}})^{-1} \qquad (6.3)$$

is the Green's function for the impurity cluster $\vec{n}-\vec{1}$ in the unperturbed crystal with band structure given by H_0. Similarly, by substituting the solution (6.2) into the equation of motion for $G_{\vec{n}-\vec{2}}$, we get an inhomogeneous equation for $G_{\vec{n}-\vec{2}}^{(nh)}$, all $\vec{n}-\vec{2}$, which is easily solved formally. Continuing this process, we can arrive at the approximate $G_0^{(nh)}$. However, the above solution of the hierarchy is, in principle, exact and is therefore examined before discussing the approximate solution. This process provides an explicit recipe for evaluating G_0 from the exact $G_{\vec{n}}$ for all $\vec{n}$, i.e.,

$$\begin{aligned}G_0=g_0+g_0\sum_{\alpha_1}\langle V_{\vec{\alpha}_1}g_{\vec{\alpha}_1}\rangle^{\vec{\alpha}_1}+\sum_{\alpha_1}\sum_{\alpha_2\neq\alpha_1}g_0\langle V_{\vec{\alpha}_1}g_{\vec{\alpha}_1}\langle V_{\vec{\alpha}_2}g_{\vec{\alpha}_1\vec{\alpha}_2}\rangle^{\vec{\alpha}_2}\rangle^{\vec{\alpha}_1}\\ +g_0\sum_{\alpha_1}\sum_{\alpha_2\neq\alpha_1}\sum_{\alpha_3\neq\alpha_2\alpha_1}\langle V_{\vec{\alpha}_1}g_{\vec{\alpha}_1}\langle V_{\vec{\alpha}_2}g_{\vec{\alpha}_1\vec{\alpha}_2}\langle V_{\vec{\alpha}_3}g_{\vec{\alpha}_1\vec{\alpha}_2\vec{\alpha}_3}\rangle^{\vec{\alpha}_3}\rangle^{\vec{\alpha}_2}\rangle^{\vec{\alpha}_1}+\cdots\\ +\sum_{\alpha_i,\,i=1,\ldots,n\;\alpha_i\neq\alpha_{i-1},\ldots,\alpha_1}g_0\langle V_{\vec{\alpha}_1}g_{\vec{\alpha}_1}V_{\vec{\alpha}_2}g_{\vec{\alpha}_1\vec{\alpha}_2}\cdots V_{\vec{\alpha}_n}G_{\vec{\alpha}_1\vec{\alpha}_2\cdots\vec{\alpha}_n}\rangle^{\vec{\alpha}_1\vec{\alpha}_2\cdots\vec{\alpha}_n}\,,\end{aligned} \qquad (6.4)$$

where $G_{\vec{n}}=\langle\mathcal{G}\rangle_{\vec{n}}$. We can alternately take $\vec{n}=\vec{N}$, with $G_{\vec{N}}\rightarrow g_{\vec{N}}=\mathcal{G}$ to obtain an exact multiple-scattering expansion of $\langle\mathcal{G}\rangle$, where terms are classified as involving scattering of 0, 1, 2, 3, ..., N sites with the random potentials $V_{\vec{\alpha}_i}$. To our knowledge, this multiple-scattering expansion has not previously been used, but it is similar in spirit to the usual T-matrix expansion, merely being a more highly summed version. For comparison, we can introduce the set of conditional scattering matrices

$$t_{\vec{\alpha}_1\cdots\vec{\alpha}_{i-1}}^{\vec{\alpha}_i}=V_{\vec{\alpha}_i}(1-g_{\vec{\alpha}_1\cdots\vec{\alpha}_{i-1}}V_{\vec{\alpha}_i})^{-1} \qquad (6.5)$$

to describe the scattering-off $\vec{\alpha}_i$ in the presence of the "impurities" $\vec{\alpha}_i\cdots\vec{\alpha}_{i-1}$. Using (6.5), Eq. (6.4) can be rewritten as

$$\begin{aligned}G_0=g_0+g_0\sum_{\alpha_1}\langle t^{\vec{\alpha}_1}\rangle^{\vec{\alpha}_1}g_0+g_0\sum_{\alpha_1}\sum_{\alpha_2\neq\alpha_1}\langle t^{\vec{\alpha}_1}g_0\langle t_{\vec{\alpha}_1}^{\vec{\alpha}_2}\rangle^{\vec{\alpha}_2}g_{\vec{\alpha}_1}\rangle^{\vec{\alpha}_1}\\ +g_0\sum_{\alpha_1}\sum_{\alpha_2\neq\alpha_1}\sum_{\alpha_3\neq\alpha_1,\alpha_2}\langle t^{\vec{\alpha}_1}g_0\langle t_{\vec{\alpha}_1}^{\vec{\alpha}_2}g_{\vec{\alpha}_1}\langle t_{\vec{\alpha}_1\vec{\alpha}_2}^{\vec{\alpha}_3}\rangle^{\vec{\alpha}_3}g_{\vec{\alpha}_1\vec{\alpha}_2}\rangle^{\vec{\alpha}_2}\rangle^{\vec{\alpha}_1}+\cdots\\ +\sum_{\alpha_i,\,i=1,\ldots,n\;\alpha_i\neq\alpha_{i-1},\ldots,\alpha_1}g_0\langle t^{\vec{\alpha}_1}g_0t_{\vec{\alpha}_1}^{\vec{\alpha}_2}\cdots t_{\vec{\alpha}_1\cdots\vec{\alpha}_{n-2}}^{\vec{\alpha}_{n-1}}g_{\vec{\alpha}_1\cdots\vec{\alpha}_{n-2}}V_{\vec{\alpha}_n}G_{\vec{\alpha}_1\cdots\vec{\alpha}_n}\rangle^{\vec{\alpha}_1\cdots\vec{\alpha}_n}\,,\end{aligned} \qquad (6.6)$$

where the last term has been left in terms of $G_{\vec{n}}$. Equation (6.6) is exact for $G_{\vec{n}}$ exact, and for $\vec{n}=\vec{N}$, the last term is

$$V_{\vec{\alpha}_N}G_{\vec{N}}\rightarrow t_{\vec{\alpha}_1,\ldots,\vec{\alpha}_{N-1}}^{\vec{\alpha}_N}g_{\vec{\alpha}_1,\cdots\vec{\alpha}_{N-1}}\,.$$

Thus, (6.4) and (6.6) can be viewed as an exact expansion in the scattering-off individual atoms or sites in the presence of clusters of all possible sizes in the background. The expansion (6.6) could probably be quite useful for low impurity concentrations, since in this case (6.6) is an expansion directly in powers of the impurity concentration.

The approximation $G_0^{(nh)}$ to G_0 is then obtained from CP$\vec{n}$ by using the CP$\vec{n}$ $G_{\vec{n}}^{(\vec{n})}$ instead of the exact $G_{\vec{n}}$ in (6.4) and/or (6.6). In using (6.4) or (6.6) in conjunction with the CP$\vec{n}$, it is necessary to have $G_{\vec{n}}^{(\vec{n})}$ for all possible $\vec{n}$. However, as discussed in Sec. V, when the cluster $\vec{n}$ is composed of disjoint parts, say $\vec{1}$ and $\vec{m}$, which are asymptotic with respect to each other, $G_{\vec{1},\vec{m}}$ may be obtained from the CP$\vec{1}$ $G_{\vec{1}}$ and the CP$\vec{m}$ $G_{\vec{m}}$, etc. The number of different clusters $\vec{n}$ for which the CP$\vec{n}$ must be obtained is thereby limited. This is to be contrasted with the approach of Aiyer *et al.*,[5] where fully self-consistent scattering by pairs of defects is treated. In the latter case, it is necessary to evaluate $\Sigma^2(R)$ and $G(R)$ (in their notation) self-consistently for all possible pairs of scatters. However, for a sufficient degree of randomness, $G(R)$ is expected to have finite coherence length R_0, so that for $R > R_0$, the pair of atoms would represent independent noninterfering scattering centers as in the CP$\vec{2}$.

We should note also that the multiple-scattering expansion used by Takeno[12] is a more highly summed version of the exact form of (6.6) with $n = N$.

The exact expansion (6.4) and (6.6) for $n = N$ is expressed in terms of the bare Green's functions g_0, and it is well known that it requires quite elaborate calculations to get even the CPA from the usual T-matrix expansion.[14] Thus, we can reexpress the exact expansion in terms of perturbed propagators, thereby making connection with recently suggested extensions of the CPA. The simplest improvement of the propagators is obtained by considering the unspecified complex self-energy σ, which is written formally as a sum of potentials originating from each site

$$\sigma = \textstyle\sum_\alpha \sigma^{(\alpha)} \quad . \tag{6.7}$$

The cluster hierarchy (2.10) can be written *exactly* as

$$[E - H_0 - V_{\vec{n}} - \sigma_{\vec{n}}]\, G_{\vec{n}} - \sum_{\alpha \notin \vec{n}} \langle (V_{\vec{\alpha}} - \sigma^{(\alpha)})\, G_{\vec{n},\vec{\alpha}} \rangle^{\vec{\alpha}} = 1 \quad , \tag{6.8}$$

where

$$\sigma_{\vec{n}} \equiv \sum_{\alpha \in \vec{n}} \sigma^{(\alpha)} \quad . \tag{6.9}$$

Equation (6.8) follows directly from (2.10) because

$$\langle \sigma^{(\alpha)}\, G_{\vec{n},\vec{\alpha}} \rangle^{\vec{\alpha}} \equiv \sigma^{(\alpha)}\, G_{\vec{n}} \quad , \tag{6.10}$$

since $\sigma^{(\alpha)}$ is taken as independent of the specification of α. Defining the perturbed Green's functions

$$\gamma_{\vec{m}} = [E - H_0 - V_{\vec{m}} - \sigma_{\vec{m}}]^{-1} \tag{6.11}$$

and the perturbed conditional T matrices

$$\tau^{\vec{\alpha}_i}_{\vec{\alpha}_1 \cdots \vec{\alpha}_{i-1}} = (V_{\vec{\alpha}_i} - \sigma^{(\alpha_i)})[1 - \gamma_{\vec{\alpha}_1 \cdots \vec{\alpha}_{i-1}}(V_{\vec{\alpha}_i} - \sigma^{(\alpha_i)})]^{-1} \quad , \tag{6.12}$$

the expansion (6.6) can be obtained in partially dressed form as

$$\begin{aligned} G_0 = {} & \gamma_0 + \gamma_0 \sum_{\alpha_1} \langle \tau^{\vec{\alpha}_1} \rangle^{\vec{\alpha}_1} \gamma_0 + \gamma_0 \sum_{\alpha_1} \sum_{\alpha_2 \neq \alpha_1} \langle \tau^{\vec{\alpha}_1} \gamma_0 \langle \tau^{\vec{\alpha}_2}_{\vec{\alpha}_1} \rangle^{\vec{\alpha}_2} \gamma_{\vec{\alpha}_1} \rangle^{\vec{\alpha}_1} \\ & + \gamma_0 \sum_{\alpha_1} \sum_{\alpha_2 \neq \alpha_1} \sum_{\alpha_3 \neq \alpha_2, \alpha_1} \langle \tau^{\vec{\alpha}_1} \gamma_0 \langle \tau^{\vec{\alpha}_2}_{\vec{\alpha}_1} \gamma_{\vec{\alpha}_1} \langle \tau^{\vec{\alpha}_3}_{\vec{\alpha}_1 \alpha_2} \rangle^{\vec{\alpha}_3} \gamma_{\vec{\alpha}_1 \vec{\alpha}_2} \rangle^{\vec{\alpha}_2} \rangle^{\vec{\alpha}_1} + \cdots \\ & + \sum_{\alpha_i,\, i=1,\ldots,n\, \alpha_i \neq \alpha_{i-1},\ldots,\alpha_1} \gamma_0 \langle \tau^{\vec{\alpha}_1} \gamma_0 \tau^{\vec{\alpha}_2}_{\vec{\alpha}_1} \cdots \tau^{\vec{\alpha}_{n-1}}_{\vec{\alpha}_1 \cdots \vec{\alpha}_{n-2}} \gamma_{\vec{\alpha}_1 \cdots \vec{\alpha}_{n-2}} (V_{\vec{\alpha}_n} - \sigma^{(\alpha_n)})\, G_{\vec{\alpha}_1 \cdots \vec{\alpha}_n} \rangle^{\vec{\alpha}_2 \cdots \vec{\alpha}_1} \quad . \end{aligned} \tag{6.13}$$

If we choose $n = N$, the last term in (6.13) contains

$$(V_{\vec{\alpha}_N} - \sigma^{(\alpha_N)})\, G_{\vec{N}} = \tau^{\vec{\alpha}_N}_{\vec{N}-\vec{1}}\, G_{\vec{N}-\vec{1}} \;, \tag{6.13$'$}$$

while for the CP$\vec{n}$ approximation $G_0^{(nh)}$,

$$G_{\vec{\alpha}_1 \cdots \vec{\alpha}_n} \rightarrow G^{(\vec{\alpha}_1 \cdots \vec{\alpha}_n)}_{\vec{\alpha}_1 \cdots \vec{\alpha}_n}$$

in (6.13). The simple CPA is obtained from (6.13) by requiring

$$\langle \tau^{\vec{\alpha}_1} \rangle^{\vec{\alpha}_1} = 0 \tag{6.14}$$

as the self-consistency requirement for $\sigma^{(\alpha)}$, and taking

$$G_0 \simeq \gamma_0 \;\; (\text{CPA}) \; . \tag{6.15}$$

The lowest-order corrections considered by Soven are the two-site scattering terms, and these are just the third term (with $\tau^{\vec{\alpha}_1} \gamma_0 \langle \tau^{\vec{\alpha}_2}_{\vec{\alpha}_1} \rangle^{\vec{\alpha}_2} \gamma_{\vec{\alpha}_1}$) of (6.13). An improved approximation to the CPA has been suggested by Schwartz and Suzuki using multiple-scattering and diagrammatic techniques, respectively.[15] In this approach, the self-energy σ is determined by the self-consistency requirement that all average single- and two-atom scattering vanish, i.e., in terms of our expansion

$$\left\langle \tau^{\vec{\alpha}_1} + \tau^{\vec{\alpha}_1} \gamma_0 \sum_{\alpha_2 \neq \alpha_1} \langle \tau^{\vec{\alpha}_2}_{\vec{\alpha}_1} \rangle^{\vec{\alpha}_2} \gamma_{\vec{\alpha}_1} \right\rangle^{\vec{\alpha}_1} = 0 \;\; (\text{CP2A}). \tag{6.16}$$

This approximation is similar in spirit to that of Aiyer *et al.*,[5] and as mentioned in relation to that work, because of the finite coherence length R_0 of γ_0, with a suitably chosen σ, for $R_{\alpha_1 \alpha_2} > R_0$,

$$(\alpha_1|\gamma_0|\alpha_2)\rightarrow 0,\quad R_{\alpha_1\alpha_2}>R_0 \tag{6.17}$$

(6.16) becomes

$$\langle\tau^{\vec{\alpha}_1}+\tau^{\vec{\alpha}_1}\gamma_0\sum_{\alpha_2\neq\alpha_1 R_{\alpha_1\alpha_2}<R_0}\langle\tau_{\vec{\alpha}_1}{}^{\vec{\alpha}_2}\rangle^{\vec{\alpha}_2}\gamma_{\vec{\alpha}_1}\rangle^{\vec{\alpha}_1}=0 \qquad (\text{CP2A}). \tag{6.18}$$

Note that the restriction in (6.18) to $R_{\alpha_1\,\alpha_2}<R_0$ reduces the apparently intractable summation over all possible pairs to a summation over a finite number of pairs. In highly disordered systems, where R_0 is quite small, (6.18) may even be tractable. As Suzuki noted, a next approximation would be obtained by self-consistently determining σ such that all one-, two-, and three-atom average scatterings vanish, etc.[15] We note again that the finite coherence length of γ_0, etc., restricts the summation over α_2 and α_3 in the three-atom term of (6.13) to those which satisfy $R_{\alpha_1\alpha_2}$, $R_{\alpha_2\alpha_3}<R_0$.

However, we now note that the introduction of the proper self-energy of (6.7) into the hierarchy as in (6.8), is far from the most general use of perturbed propagators. The $\sigma_{\vec{n}}$ in (6.8) makes specific reference to the cluster $\vec{n}$ only insofar as it does not contain contributions from atoms on $\vec{n}$. Furthermore, the same $\sigma^{(\alpha)}$ is used in the auxiliary propagators $\gamma_{\vec{n}}$, $\gamma_{\vec{n}-\vec{1}}$, $\cdots$, γ_0. Such a choice is, of course, motivated by a desire to obtain the exact proper self-energy of $\langle G\rangle$, so that if $\sigma^{(\alpha)}$ were chosen to be the self-energy of G_0 in any approximate theory, the result is a self-consistency requirement for the approximate proper self-energy. However, on physical grounds it is expected that the proper self-energy, say $s_{\vec{n}}{}^{(\alpha)}$, of the exact $G_{\vec{n}}$ would differ from that (i.e., $s_0^{(\alpha)}$) of the exact G_0 in the neighborhood of the cluster $\vec{n}$. This arises because the information concerning the specification of the cluster $\vec{n}$ propagates over distances of the order of R_0. Thus, we expect greater accuracy and rapidity of convergence of the multiple-scattering expansion if the approximate proper self-energy $s_{\vec{n}}$ reflects this dependence.

Explicitly, let

$$s_{\vec{n}}=\sum_{\alpha\notin\vec{n}}s_{\vec{n}}{}^{(\alpha)} \tag{6.19}$$

be a decomposition of the $\vec{n}$th auxiliary proper self-energy into contributions from each site in some as yet unspecified manner. $s_{\vec{n}}^{(\alpha)}$ depends upon the random potential $V_{\vec{n}}$ of the cluster $\vec{n}$, but not upon the random potential of the site α. Furthermore, in general,

$$s_{\vec{n}}^{(\alpha)}\neq s_{\vec{m}}^{(\beta)},\quad \alpha,\ \beta\notin\vec{n},\vec{m},\quad \text{all } \vec{n},\vec{m} \tag{6.20}$$

so that there is maximum freedom of choice of $\{s_{\vec{n}}^{(\alpha)},\ \text{all } \vec{n},\alpha\}$ to speed up convergence and maintain internal self-consistency. Defining the new perturbed propagators

$$\Gamma_{\vec{m}}=(E-H_0-V_{\vec{m}}-s_{\vec{n}})^{-1}, \tag{6.21}$$

the exact cluster hierarchy can formally be solved to give the exact cluster series

$$G_0=\Gamma_0+\Gamma_0\sum_{\alpha_1}\langle(V_{\vec{\alpha}_1}-s_0^{(\alpha_1)})\Gamma_{\vec{\alpha}_1}\rangle^{\vec{\alpha}_1}+\Gamma_0\sum_{\alpha_1}\Big\langle(V_{\vec{\alpha}_1}-s_0^{(\alpha_1)})\Gamma_{\vec{\alpha}_2}\sum_{\alpha_2\neq\alpha_1}\langle(V_{\vec{\alpha}_2}-s_{\vec{\alpha}_1}^{(\alpha_2)})\Gamma_{\vec{\alpha}_1\vec{\alpha}_2}\rangle^{\vec{\alpha}_2}\Big\rangle^{\vec{\alpha}_1}$$
$$+\Gamma_0\sum_{\alpha_1}\Big\langle(V_{\vec{\alpha}_1}-s_0^{(\alpha_1)})\Gamma_{\vec{\alpha}_1}\sum_{\alpha_2\neq\alpha_1}\Big\langle(V_{\vec{\alpha}_2}-s_{\vec{\alpha}_1}^{(\alpha_2)})\,\Gamma_{\vec{\alpha}_1\vec{\alpha}_2}\sum_{\alpha_3\neq\alpha_1,\alpha_2}\langle(V_{\vec{\alpha}_3}-s_{\vec{\alpha}_1\vec{\alpha}_2}^{(\alpha_3)})\,\Gamma_{\vec{\alpha}_1\vec{\alpha}_2\vec{\alpha}_3}\rangle^{\vec{\alpha}_3}\Big\rangle^{\vec{\alpha}_2}\Big\rangle^{\vec{\alpha}_1}+\cdots$$
$$+\Gamma_0\sum_{\alpha_i,\,i=1,\cdots,k\ \alpha_i\neq\alpha_{i-1},\cdots\alpha_i}(V_{\vec{\alpha}_1}-s_0^{(\alpha_1)})\Gamma_{\vec{\alpha}_1}\cdots(V_{\vec{\alpha}_k}-s_{\vec{k}-\vec{1}}^{(\alpha_k)})\ \ G_{\vec{\alpha}_1\ldots\vec{\alpha}_k}\rangle^{\vec{\alpha}_1\cdots\vec{\alpha}_k}, \tag{6.22}$$

where $G_{\vec{k}}$ is the exact cluster Green's function. Because of (6.20), it is more convenient to leave (6.22) in terms of the potentials $V_{\vec{\alpha}}-s^{(\alpha)}$ than to introduce conditional T matrices as in (6.5) and (6.12). However, (6.22) can still be considered to be an exact multiple-scattering expansion. [Note that we are free to choose $\vec{k}=\vec{N}$, and then in (6.22) $G_{\vec{N}}=\mathcal{G}$, the unaveraged Green's function.]

For the case $\vec{k}=\vec{N}$, the freedom of choice of $s_{\vec{m}}$, $m=1,\cdots,n$, enables us to make all the terms of the exact series (6.22) involving $1,2,\cdots,n$ atom cluster scattering vanish *for any choice of* $\Gamma_{\vec{n}}$. However, we now demonstrate how the use of the CP$\vec{n}$ approximation in (6.22) can be used to explicitly generate *the optimum approximation* in which $G_0=\Gamma_0$ and terms which involve scattering-off clusters of size $n+1$. The final result, therefore, is an explicit recipe for the evaluation of s_0 from quantities obtained self-consistently from CP$\vec{n}$, as well as an explicit representation of the lowest-order corrections. Consider the term in (6.22) involving scattering-off n-atom clusters. A sufficient condition for the vanishing of this term is that the average scattering-off of the nth atom vanishes, i.e.,

$$\sum_{\alpha\notin\vec{n}-\vec{1}}\langle(V_{\vec{\alpha}}-s_{\vec{n}-1}^{(\alpha)})\Gamma_{\vec{n}-\vec{1},\vec{\alpha}}\rangle^{\vec{\alpha}}=0,\quad \text{all } \vec{n}-\vec{1}. \tag{6.23}$$

A sufficient condition for the vanishing of (6.23) is that the summand vanish for all α:

$$\langle((V_{\vec{\alpha}}-s^{(\alpha)}_{\vec{n}-\vec{1}})\Gamma_{\vec{n}-\vec{1},\vec{2}\,\vec{\alpha}}\rangle^{\vec{\alpha}}=0 \quad \text{all } \vec{n}-\vec{1},\ \alpha\notin\vec{n}-\vec{1}. \tag{6.24}$$

If $\Gamma_{\vec{n}-\vec{1},\vec{\alpha}}$ were taken as the CP$\vec{n}$ $G^{(\vec{n}-\vec{1},\vec{\alpha})}_{\vec{n}-\vec{1},\vec{\alpha}}$, then by (4.14a) and (4.4),

$$\langle((V_{\vec{\alpha}}-s^{(\alpha)}_{\vec{n}-\vec{1}})\Gamma_{\vec{n}-\vec{1},\vec{\alpha}}\rangle^{\vec{\alpha}}=\sigma^{(\alpha)}_{\vec{n}-\vec{1}}(\vec{n}-\vec{1},\vec{\alpha})\,G^{(\vec{n}-\vec{1},\vec{\alpha})}_{\vec{n}-\vec{1}} - s^{(\alpha)}_{\vec{n}-\vec{1}}\,G^{(\vec{n}-\vec{1},\vec{\alpha})}_{\vec{n}-\vec{1}}, \tag{6.25}$$

where $G^{(\vec{n}-\vec{1},\vec{\alpha})}_{\vec{n}-\vec{1}}$ and $\sigma^{(\alpha)}_{\vec{n}-\vec{1}}(\vec{n}-\vec{1},\vec{\alpha})$ denote the $(n-1)$ cluster Green's function and proper self-energy as obtained from CP$\vec{n}-\vec{1}$, i.e.,

$$G^{(\vec{n}-\vec{1},\vec{\alpha})}_{\vec{n}-\vec{1}}=\langle G^{(\vec{n}-\vec{1},\vec{\alpha})}_{\vec{n}-\vec{1},\vec{\alpha}}\rangle^{\vec{\alpha}}$$

$$\equiv\Big(E-H_0-V_{\vec{n}-\vec{1}}-\sum_{\beta\notin\vec{n}-\vec{1}}\sigma^{(\beta)}_{\vec{n}-\vec{1}}(\vec{n}-\vec{1},\vec{\alpha})\Big)^{-1}. \tag{6.26}$$

Thus, if we take

$$s^{(\alpha)}_{\vec{n}-\vec{1}}=\sigma^{(\alpha)}_{\vec{n}-\vec{1}}(\vec{n}-\vec{1},\vec{\alpha}),\quad \text{all } \vec{n}-\vec{1},\quad \alpha\notin\vec{n}-\vec{1} \tag{6.27}$$

then (6.24) and (6.23) are satisfied identically, so that the n-atom scattering term of (6.23) vanishes identically. We note that if the site α is asymptotically far from the cluster $\vec{n}-\vec{1}$ so that $\sigma^{(\alpha)}_{\vec{n}-\vec{1}}(\vec{n}-\vec{1},\vec{\alpha})$ is sensible independent of $\vec{n}-\vec{1}$,

$$s^{(\alpha)}_{\vec{n}-\vec{1}}\rightarrow\sigma_0^{(\alpha)}(\vec{\alpha}),\quad R_{\alpha\vec{n}-\vec{1}}>R_0\,. \tag{6.28}$$

This is the CP$\vec{1}$ approximation in which there is direct account of correlations between site α and its neighbors which are within the coherence range. We note that in order to obtain $s^{(\alpha)}_{\vec{n}-\vec{1}}$, all $\vec{n}-\vec{1}$, $\alpha\notin\vec{n}-\vec{1}$, the CP$\vec{n}$ $G^{(\vec{n})}_{\vec{n}}$ is required for all $\vec{n}$. However, because of the asymptotic properties of noncompact clusters (5.11), there are only a finite number of translationally inequivalent clusters $\vec{n}$ to be considered.

Now that $\Gamma_{\vec{n}}$ and $s_{\vec{n}-\vec{1}}$ have been specified, $\Gamma_{\vec{n}-\vec{1}}$ is given by (6.21), but we can choose $s_{\vec{n}-\vec{2}}$ such that the term in (6.22) which involves scattering-off of $(n-1)$ atom clusters also vanishes. A sufficient condition for this term to vanish is

$$\langle((V_{\vec{\alpha}}-s^{(\alpha)}_{\vec{n}-\vec{2}})\Gamma_{\vec{n}-\vec{2},\vec{\alpha}}\rangle^{\vec{\alpha}}=0,\quad \text{all } \vec{n}-\vec{2},\ \alpha\notin\vec{n}-\vec{2} \tag{6.29}$$

or

$$s^{(\alpha)}_{\vec{n}-\vec{2}}=\langle V_{\vec{\alpha}}\Gamma_{\vec{n}-\vec{2},\vec{\alpha}}\rangle^{\vec{\alpha}}(\langle\Gamma_{\vec{n}-\vec{2},\vec{\alpha}}\rangle^{\vec{\alpha}})^{-1},\quad \text{all } \vec{n}-\vec{2},\ \alpha\notin\vec{n}-\vec{2}\,. \tag{6.30}$$

By induction, all terms involving m-atom scattering $1\le m\le n$, can be made to vanish by choosing

$$s^{(\alpha)}_{\vec{m}}=\langle V_{\vec{\alpha}}\Gamma_{\vec{m},\vec{\alpha}}\rangle^{\vec{\alpha}}(\langle\Gamma_{\vec{m},\vec{\alpha}}\rangle^{\vec{\alpha}})^{-1},\quad \text{all } \vec{m},\ \alpha\notin\vec{m}. \tag{6.31}$$

In particular, (6.31) along with (6.27) for $m=n$, gives an explicit prescription for the evaluation of a translationally invariant approximation to G_0, namely, Γ_0, from the CP$\vec{n}$, for which the lowest-order corrections involve the scattering-off of $(n+1)$ atom clusters. This lowest-order correction could, in principle, be evaluated once some approximation $\Gamma_{\vec{n}+1}$ is chosen. By taking $\Gamma_{\vec{n},\vec{\alpha}}$ in terms like $\langle((V_{\vec{\alpha}}-s^{(\alpha)}_{\vec{n}})\Gamma_{\vec{n},\vec{\alpha}}\rangle^{\vec{\alpha}}$ to be $G^{\vec{\alpha}\,(\vec{n})}_{\vec{n}}$, we could make the $(n+1)$ atom scattering vanish. However, as this procedure is not invariant, i.e., $\vec{\alpha}$ is treated differently from $\vec{n}$, it simply relegates the $(n+1)$ atom scattering formally to the higher-order scattering terms.

For arbitrary $\Gamma_{\vec{n}}$ (all $\vec{n}$), the recipe (6.31) for $m=0,\dots,\ n-1$ makes all the $(1,\dots,n)$-atom cluster terms in the series (6.22) vanish. From (6.22), we see, however, that the optimum choice of $\Gamma_{\vec{n}}$ is that which represents the best approximation to the exact $G_{\vec{n}}$, and this is taken as the CP$\vec{n}$ $G^{(\vec{n})}_{\vec{n}}$.

As in the case of ECP$\vec{n}$, it would be desirable to utilize the information which is contained in CP$\vec{n}$ more fully by considering a set of specified clusters of size n which are distributed densely throughout space. The set of $G^{(\vec{n}_1,\vec{n}_2,\dots;\,n_j\dots)}_{\vec{n}_1,\vec{n}_2,\dots;\,\vec{n}_j,\dots}$ so obtained could then be introduced into the expansion (6.22). If the summations are then restricted to involve all translationally equivalent cluster distributions of this type, the above formalism could be used to generate a set of $\Gamma_{\vec{m}}$, etc., for which all scattering-off of these types of clusters vanishes. However, because of the asymptotic properties of the clusters with respect to each other,

$$V_{\vec{\alpha}}G^{(\vec{n}_1,\dots,\vec{n}_j,\dots)}_{\vec{n}_1;\dots,\vec{n}_j-\vec{1},\vec{\alpha},\dots}\rightarrow V_{\vec{\alpha}}G^{(\vec{n}_j-\vec{1},\vec{\alpha})}_{\vec{n}_j-\vec{1},\vec{\alpha}}, \tag{6.32}$$

and all these higher-order n-atom cluster terms also vanish in (6.22) when the simple CP$\vec{n}$ $G^{(\vec{n})}_{\vec{n}}$ is chosen for $\Gamma_{\vec{n}}$. Thus, the corrections arising from m atom scattering, $m\ge n+1$, imply scattering from compact clusters only.

The averaging via the equations of motion has been shown to lead to some highly compact and flexible exact formulations of multiple-scattering theory. When used in conjunction with the CP$\vec{n}$, it provides a formal solution to the problem of correctly accounting for the scattering-off of all compact n-atom clusters. This averaging procedure would appear to be superior to the ECP$\vec{n}$ since the former does not have the underlying analytic structure as the latter does. Thus, CPnh should be capable of providing renormalized band edges in addition to localized states; however, because of its more general analytic structure we cannot formally give explicit proofs of these expected results. CP1h or CP2h calculations would therefore be of interest, although they are not necessary for the present development.

VII. REMARKS ON BOUND STATES

A central problem in the theory of the electronic band structure in disordered systems concerns the existence and nature of bound, or localized, states in the band tails. In the CP$\vec{n}$ approximation, and hence in ECP$\vec{n}$, the existence of such bound states in the band tails follows directly from the asymptotic properties of CP$\vec{n}$ and the known properties of CPA.

In CP$\vec{n}$, if we obtain $G_0^{(\vec{n})}$ from $G_{\vec{n}}$ via the simple averaging

$$G_0^{(\vec{n})} = \langle G_{\vec{n}}^{(\vec{n})} \rangle^{\vec{n}} , \qquad (7.1)$$

where in the case of the one-band model used in the CPA, the averaging in (6.1) is discrete, (with v_α not necessarily limited to two values) so that any localized states, i.e., discrete poles, which occur in $G_{\vec{n}}^{(\vec{n})}$ for any composition $\vec{n}$ also appear in $G_0^{(\vec{n})}$. Similarly, any discrete poles in any $G_{\vec{n}}^{(\vec{n})}$ also must occur in $G_0^{(n_i)}$ of (5.13), even if there are states in $G_0^{(n_i)}$ which are everywhere dense in that particular energy range. Thus, it is sufficient to consider the existence and nature of bound states in $G_{\vec{n}}$ only in the CP$\vec{n}$ approximation.

The poles of $G_{\vec{n}}(E)$ are determined by the solution of

$$\det \left| G_{\vec{n}}^{-1}(E) \right| = 0 . \qquad (7.2)$$

Because of the asymptotic limits of CP$\vec{n}$ as discussed in Sec. IV C, we can convert the infinite-rank determinant of (7.2) to one of only finite rank by multiplying (7.2) by $\det | G_A(E) |$. The result is just

$$\det \left| 1 - G_A(E) U_{\vec{n}A}(E) \right| = 0, \qquad (7.3)$$

where $U_{\vec{n}A}(E)$ is given by (4.28c) and (4.30) and, because of (4.29), is a matrix of finite rank centered around the cluster $\vec{n}$.

We already know that $\mathrm{Im}\, G_0(E^+)$ is nonzero only within bounded ranges of E according to the localization theorem.[1,16] In the regions outside of the CPA band for which $\mathrm{Im}\, G_A(E^+)$ vanishes, we have

$$\mathrm{Im}\, \sigma_A(E^+) = 0. \qquad (7.4)$$

In energy regions which satisfy (7.4), we shall now demonstrate that $U_{\vec{n}A}(E^+)$ is also real. Solutions to (7.3) can therefore occur for real energies E^+, thereby leading to bound states which are between the CPA band edges and the limit allowed by the localization theorem. The finite extent of $U_{\vec{n}A}(E^+)$ already implies the localization of these states.

From the self-consistency equation for $\sigma_{\vec{n}}^{(\alpha)}(E)$ in (4.23), it is clear that $\sigma_{\vec{n}}^{(\alpha)}(E)$ is continuous across any poles in $(\alpha | G_{\vec{n}}^{\vec{\alpha}}(E) | \alpha)$. The only singularities that may occur in $\sigma_{\vec{n}}^{(\alpha)}(E)$ come from the vanishing of the denominator in (4.23) and require

$$(\alpha | G_{\vec{n}}(E) | \alpha) \equiv 1/(\alpha | \sigma_{\vec{n}}^{(\alpha)}(E) | \alpha) \equiv 0 . \qquad (7.5)$$

This can only occur at isolated points, say between bands, but can be discounted as a general occurrence in the band tails. In practice, (4.23) can be solved self-consistently by taking as the first approximation

$$\sigma_{\vec{n}}^{(\alpha;1)}(E) = \frac{\langle v_{\vec{\alpha}} + v_{\vec{\alpha}} (\alpha | G_A^{\vec{n}\vec{\alpha}}(E) | \alpha) v_{\vec{\alpha}} \rangle^{\vec{\alpha}}}{1 + \langle v_{\vec{\alpha}} (\alpha | G_A^{\vec{n}\vec{\alpha}}(E) | \alpha) \rangle^{\vec{\alpha}}} , \qquad (7.6)$$

where

$$G_A^{\vec{n}\vec{\alpha}}(E) = \Bigl(E - H_0 - \sigma_A - \sum_{\vec{\beta} \in \vec{n}, \alpha} (V_{\vec{\beta}} - \sigma_A^{(\beta)}) \Bigr)^{-1} \qquad (7.7)$$

is the zeroth-order approximation to $G_{\vec{n}}^{\vec{\alpha}}$. Then using (7.6), we obtain a first-order $G_{\vec{n}}^{\vec{\alpha}}$,

$$G_{\vec{n}}^{\vec{\alpha}(1)} = [E - H_0 - \sigma_{\vec{n}}^{(1)}(E) - V_{\vec{n}} - (V_{\vec{\alpha}} - \sigma_{\vec{n}}^{(\alpha;1)})]^{-1}, \qquad (7.8a)$$

where

$$\sigma_{\vec{n}}^{(1)} \equiv \sum_{\alpha \notin \vec{n}} \sigma_{\vec{n}}^{(\alpha;1)} . \qquad (7.8b)$$

Using (7.8) in the right-hand side of (4.23) gives a second approximation to $\sigma_{\vec{n}}^{(\alpha)}$, $\sigma_{\vec{n}}^{(\alpha;2)}$, which can be used to generate a $G_{\vec{n}}^{\vec{\alpha}(2)}$, etc., until self-consistency is achieved.

Note that (7.7) just gives rise to the Slater-Koster problem for an impurity cluster $\vec{n}$, which is embedded in a lattice whose band structure is given by the CPA. Outside the CPA band edges, since $\sigma_A(E^+)$ is real, the only singularities of (7.7) can be simple poles for real E. Preliminary calculations of (7.7) by Kirkpatrick have indeed demonstrated the existence of these poles. Therefore, (7.6) implies that $\sigma_{\vec{n}}^{(\alpha;1)}(E + i\epsilon)$ can have at most an infinitesimal imaginary part, whereupon

$$G_{\vec{n}}^{\vec{\alpha}(2)} = [E - H_0 - \sigma_{\vec{n}}^{(2)} - V_{\vec{n}} - (V_{\vec{\alpha}} - \sigma_{\vec{n}}^{(\alpha;2)})]^{-1} \qquad (7.9)$$

can only have simple poles for real E in this region. Since we assume that the asymptotic properties imply that self-consistency may be achieved to any desired accuracy in a finite number of steps, we may conclude that $\sigma_{\vec{n}}^{(\alpha)}(E)$ is real (apart from an infinitesimal imaginary part).

Thus, in CP$\vec{n}$, *we have demonstrated the existence of bound (localized) states outside of the* CPA *band edges, but in the energy region allowed by the localization theorem.* The relationship between (7.7) and the usual Slater-Koster problem immediately provides insight into the parentage of these states. In the case of the binary random alloy problem, numerical calculations are feasible and will exhibit the bound states in detail.

Although (7.3) provides the conditions for existence and then the description of the bound states, it does not directly provide any information as to their stability as the size of the cluster $\vec{n}$ increases. In other words, as n increases, in CP$\vec{n}$ do these states remain bound, or do they become extended resonancelike states? Given a bound state in CP$\vec{n}+\vec{m}$, where the state is localized completely on $\vec{m}$, with $\vec{n}$ completely surrounding $\vec{m}$, clearly this state will be totally unaffected (i.e., remain bound) by increasing the size of the cluster. On the other hand, if a bound state in CP$\vec{n}$ extends outside $\vec{n}$ into the surrounding medium, it may become extended or stay bound as the size of $\vec{n}$ is increased. A little reflection immediately provides expected cases of both types.

Our inability to treat increasingly large clusters, in general, limits CP$\vec{n}$ from determining where the transition from extended to localized states occurs and from determining the analytic properties of the electronic structure in this region. Thus, the energy region about E_c is analogous to the critical region on a thermodynamic phase diagram since the long-range potential fluctuations ultimately determine the character, bound vs extended, of the states in this energy region. This analogy between E_c and a usual critical point also is clear from the classical viewpoint of percolation theory.[17]

As we pass from CP$\vec{n}$ to ECP$\vec{n}$, we note that bound states in CP$\vec{n}$, which are localized over a spatial region which is smaller in size than R_0, must also remain bound in ECP$\vec{n}$. As in (5.10), two such bound states, on clusters $\vec{l}$ and $\vec{m}$, are totally independent, and therefore there is no tunneling or hopping between these states. In the region near the CPA band edge, however, the extent of the bound states becomes $\gtrsim R_0$, so that in ECP$\vec{n}$ bound states on neighboring clusters may overlap slightly. Hence, there is the possibility of "percolation" to extended states, and therefore ECP$\vec{n}$ will contain a transition energy, depending on cell size, which will only become accurate as the ECP$\vec{n}$ cell size and $\vec{n}\rightarrow\infty$. By analogy with critical points in ordinary statistical mechanics, it is probably necessary to have a separate theory to describe accurately the region about E_c. The ECP$\vec{n}$ therefore provides a theory which extrapolates through E_c (and the band edges), but is expected to be accurate in all other regions. Thus, ECP$\vec{n}$ is reminiscent of mean field theories (with or without the summation of the "dominant" diagrams)[18] of ferromagnetism, etc., which work well everywhere but in the neighborhood of the critical point.

---

*Supported by ARO(D), NASA, NSF, and ARPA.

†Alfred P. Sloan Foundation Fellow.

[1] (a) P. Soven, Phys. Rev. 156, 809 (1967); B. Velický, S. Kirkpatrick, and H. Ehrenreich, *ibid.* 175, 747 (1968); P. Soven, *ibid.* 178, 1136 (1969); B. Velický, *ibid.* 184, 614 (1969); S. Kirkpatrick, B. Velický, and H. Ehrenreich, *ibid.* B (to be published). (b) D. W. Taylor, *ibid* 156, 1017 (1967), has discussed the same problem with reference to vibrations in disordered systems.

[2] N. F. Mott, Advan. Phys. 16, 49 (1967); M. H. Cohen, H. Fritzsche, and S. R. Ovshinsky, Phys. Rev. Letters 22, 1065 (1969).

[3] For a review of recent work see M. H. Cohen, J. Non-Cryst. Solids 4, 391 (1970).

[4] I. M. Lifshitz, Advan. Phys. 13, 483 (1964); E. O. Kane, Phys. Rev. 131, 79 (1963); E. I. Halperin and M. Lax, *ibid.* 148, 722 (1966); J. Zittartz and J. S. Langer, *ibid.* 148, 741 (1966); J. M. Ziman, J. Phys. C 1, 1532 (1968); P. W. Anderson, Phys. Rev. 109, 1492 (1958).

[5] R. N. Aiyer, R. J. Elliott, J. A. Krumhansl, and P. L. Leath, Phys. Rev. 181, 1006 (1969).

[6] S. F. Edwards has expressed a similar point of view: S. F. Edwards, J. Phys. C 3, L30 (1970); J. Non-Cryst. Solids 4, 417 (1970).

[7] L. Nordheim, Ann. Physik 9, 607 (1931); S. F. Edwards, Proc. Roy. Soc. (London) A267, 518 (1962).

[8] L. L. Foldy, Phys. Rev. 67, 107 (1945); J. L. Levine and T. M. Sanders, *ibid.* 154, 138 (1967).

[9] M. H. Cohen, J. Non-Cryst. Solids 2, 432 (1970).

[10] E. N. Economou and M. H. Cohen, Phys. Rev. Letters 24, 218 (1970).

[11] See also N. F. Berk, Phys. Rev. B 1, 1336 (1970).

[12] S. Takeno, Progr. Theoret. Phys. (Kyoto) 40, 942 (1968); 42, 1221 (1969).

[13] W. Kohn, *Proceedings of the Third IMR Symposium on Electronic Density of States*, Natl. Bur. Std. Special Publ. No. 323 (U. S. GPO, Washington, D. C., 1970).

[14] See F. Yonezawa and T. Matsubara, Progr. Theoret. Phys. (Kyoto) 35, 357 (1966); 35, 759 (1966); P. L. Leath, Phys. Rev. 171, 725 (1968), and references therein.

[15] L. Schwartz (private communication); M. Suzuki (private communication).

[16] J. M. Luttinger, Phil. Res. Rept. 6, 303 (1951).

[17] T. P. Eggarter and M. H. Cohen, Phys. Rev. Letters 25, 807 (1970).

[18] R. Brout, *Phase Transitions* (Benjamin, New York, 1965).